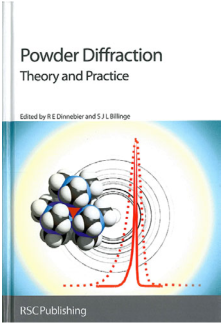
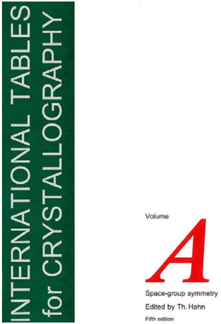
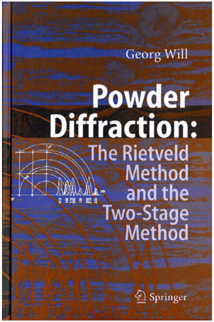
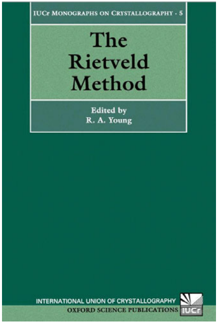
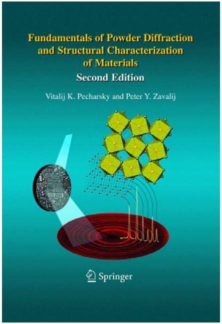
X-ray powder diffraction – a practical guide





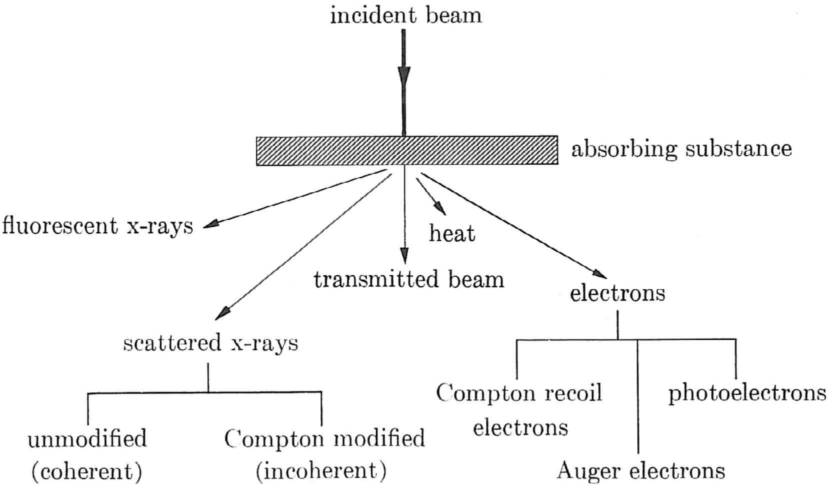






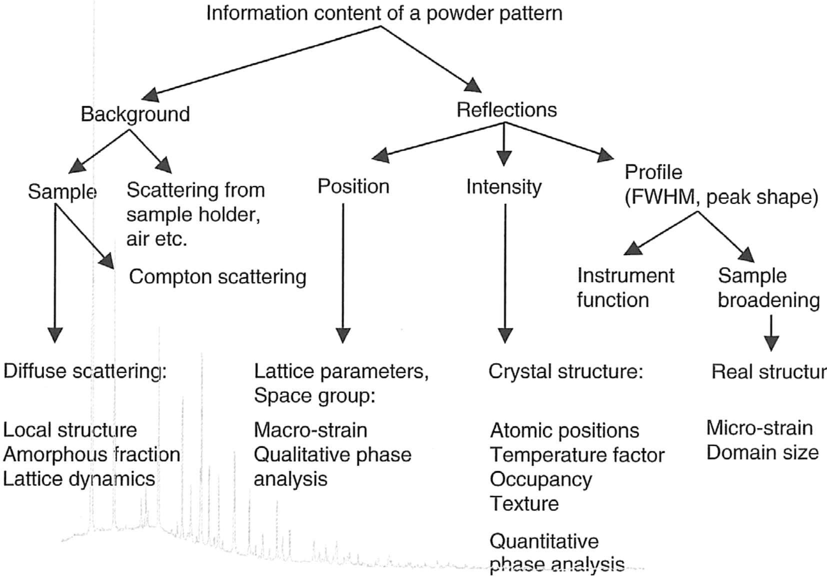
Dinnebier 0; InternationalTables 0; Will 0; Young 0; Pecharsky 0

X-ray hitting condensed matter



Cullity 114

X-ray hitting condensed matter

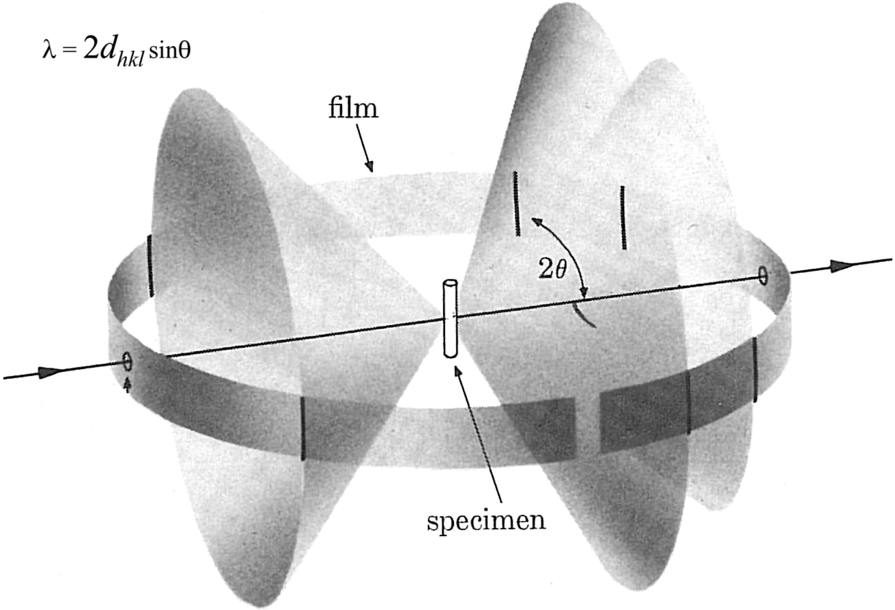


$$\lambda = 2d_{hkl}\sin\theta$$

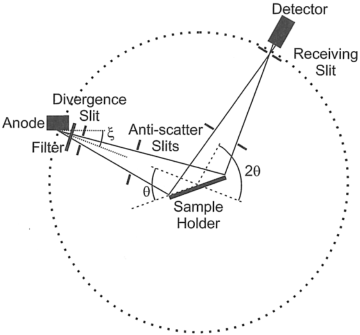
$$\mathbf{F}(\mathbf{h}) = \sum_{j=1}^{n} g^{j} t^{j}(s) f^{j}(s) \exp(2\pi i \mathbf{h} \cdot \mathbf{x}^{j})$$

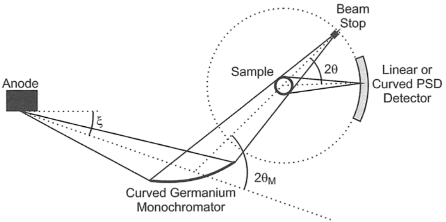
Debye-Scherrer cones from a polycrystalline sample

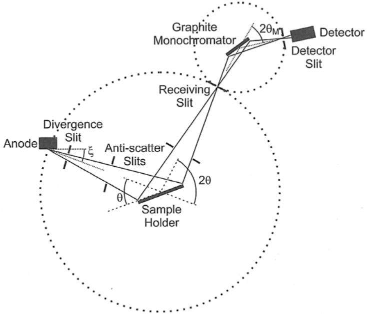
$$\lambda = 2d_{hkl}\sin\theta$$

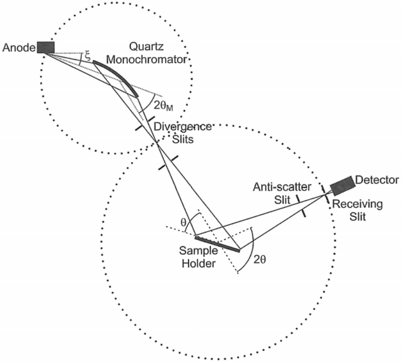


Bragg-Brentano and Guinier diffractometer



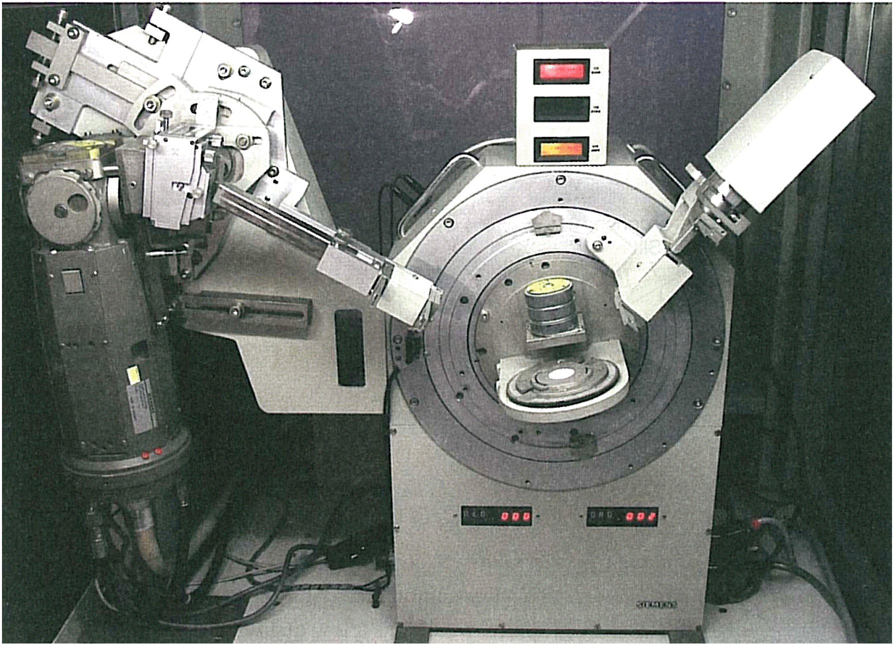




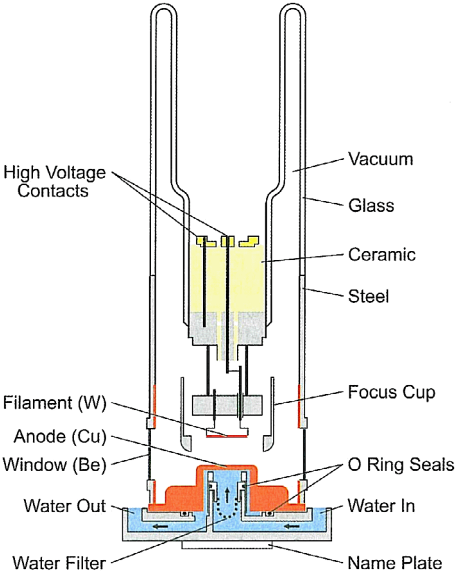


Dinnebier 34, 35_1, 35_2, 37

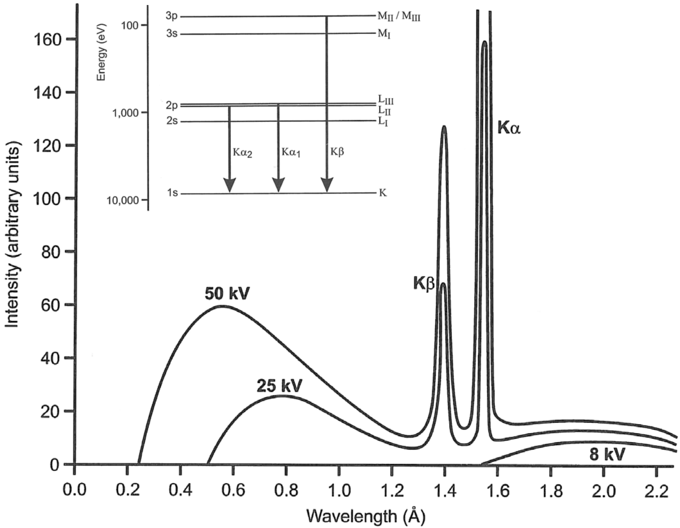
Bragg-Brentano diffractometer with monochromator



Generation of x-ray

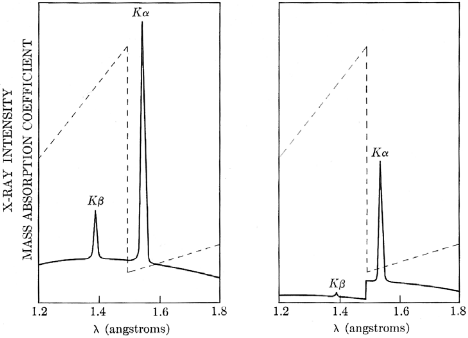


Generation of x-ray



Optimum voltage ~4 times characteristic energy (~30 kV for Cu anodes)

Generation of x-ray



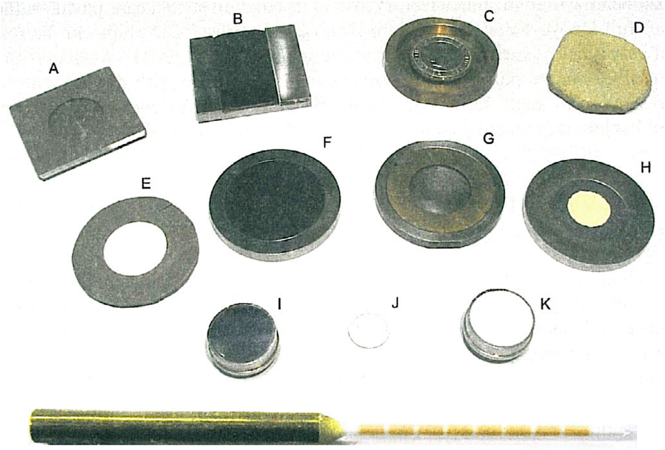
(a) No filter (b) Nickel filter

Target	Filter	Incident beam* $\frac{I(K\alpha)}{I(K\beta)}$	Filter thickness for $\frac{I(K\alpha)}{I(K\beta)} = \frac{500}{1}$ in trans. beam		$\frac{I(K\alpha)\text{ trans.}}{I(K\alpha)\text{ incident}}$
			mg/cm²	in.	
Mo	Zr	5.4	77	0.0046	0.29
Cu	Ni	7.5	18	0.0008	0.42
Co	Fe	9.4	14	0.0007	0.46
Fe	Mn	9.0	12	0.0007	0.48
Cr	V	8.5	10	0.0006	0.49

* This is the intensity ratio *at the target* [G.11, Vol. 3, p. 71]. This ratio outside the x-ray tube will be changed somewhat by the differential absorption of $K\alpha$ and $K\beta$ by the tube window, typically beryllium, 0.01 inch (0.25 mm) thick.

Suppression of *Kβ* radiation by filter with lighter neighbor element in periodic table

Samples for x-ray powder diffraction



Well prepared samples at the right sample holder is the key for success!!!

Samples for x-ray powder diffraction

Hygiene in preparing the powder is the second key for success!!!

Samples for x-ray powder diffraction

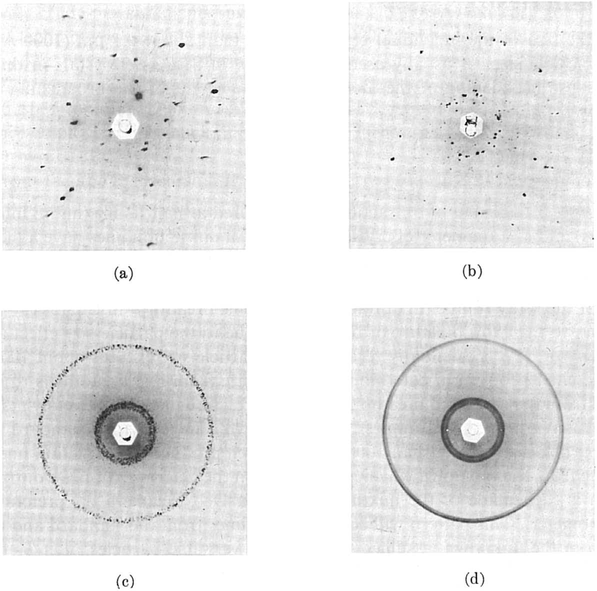


Fig. 9–1 Back-reflection pinhole patterns of recrystallized aluminum specimens; grain size decreases in the order (a), (b), (c), (d). Filtered copper radiation.

Cullity 283

Samples for x-ray powder diffraction

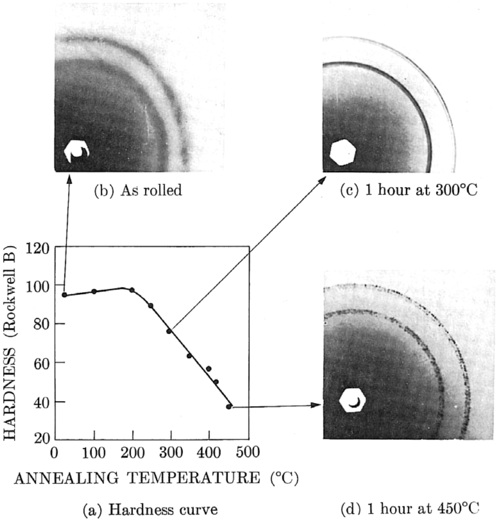
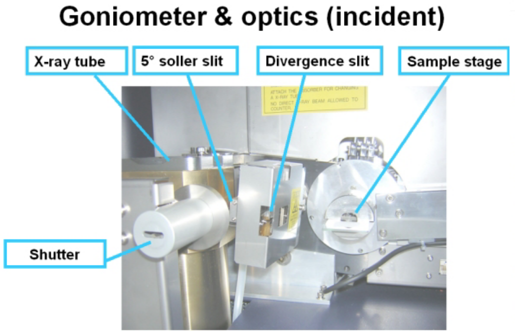
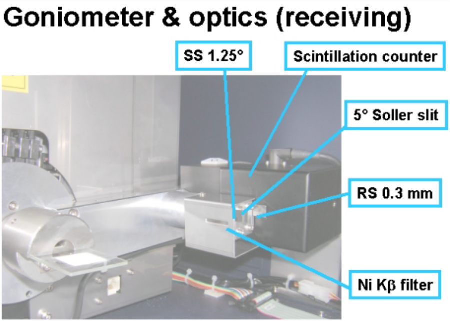


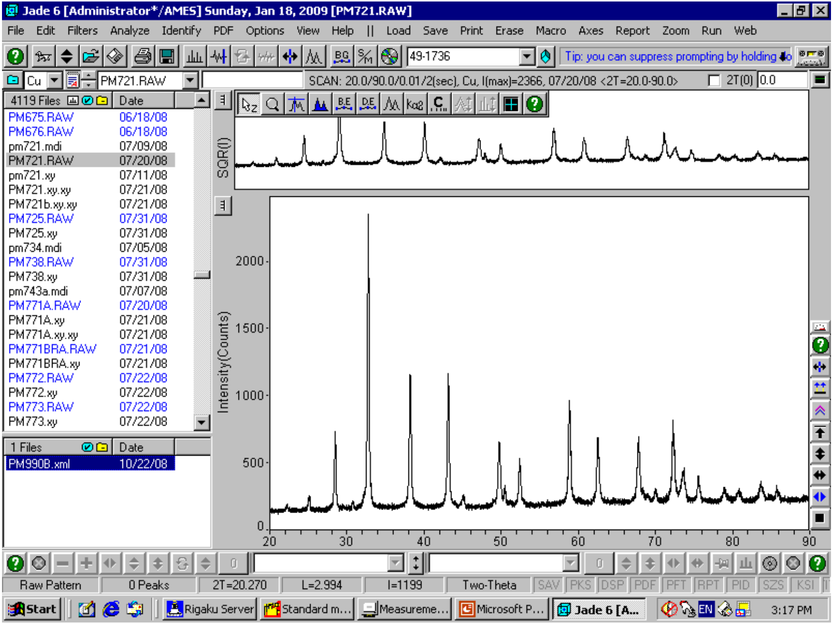
Fig. 9–3 Changes in hardness and diffraction lines of 70 Cu–30 Zn specimens, reduced in thickness by 90 percent by cold rolling, and annealed for 1 hour at the temperatures indicated in (a). (b), (c), and (d) are portions of back-reflection pinhole patterns of specimens annealed at the temperatures stated (filtered copper radiation).

Bragg-Brentano diffractometer for the desk





Example: growth of PrAuSi out of Sn flux



Which phases are present?

E. D. Mun: PM721-Ex1a

Phase analysis with the PDF database

POWDER DIFFRACTION FILE

Sets 1-5 (Revised)

Inorganic Volume, No. PD1S-5iRB

Published by the
JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS
1601 Park Lane, Swarthmore, Pennsylvania 19081
U.S.A.

1-0024 MAJOR CORRECTION

d (0068 / 1-0024)	12.8	3.60	6.9	12.8	$ZrOCl_2 \cdot 8H_2O$
I/I_1 (1-0024)	100	83	67	100	Zirconium Oxychloride octa Hydrate

Rad. MoKα λ 0.709 Filter ZrO_2
Dia. 16 inches Cut off Coll.
I/I_1 Calibrated strips d corr. abs.? No
Ref. H

Sys. Tetragonal S.G.
a_0 12.9 b_0 c_0 10.6 A C
α β γ Z
Ref. B.P. (computed from powder data)

εα nωβ 1.552 εγ 1.563 Sign +
2V D mp Color
Ref. Wa

d Å	I/I_1	hkl	d Å	I/I_1	hkl
12.8	100	100	2.07	13	
10.6	27	001	2.00	7	
7.9	20	101	1.91	13	
6.9	67	111	1.81	13	
4.80	13	102	1.71	13	
4.12	27	221	1.62	13	
3.82	20	212,311	1.57	7	
3.60	83	320	1.51	7	
3.24	40	400	1.46	7	
2.96	7	213	1.42	7	
2.74	7	402			
2.55	7	430,104			
2.39	7	520			
2.22	13	304,441			
2.15	20	600			
		Indexed by B.P.			

33-1161   33-1162

d	3.34	4.26	1.82	4.26	SiO_2 ★
I/I_1	100	22	14	22	Silicon Oxide — Quartz, low

Rad. $CuK\alpha_1$ λ 1.540598 Filter Mono. Dia.
Cut off I/I_1 Diffractometer I/I cor.
Ref. Nat. Bur. Stand. (U.S.) Monogr. 25, Sec. 18 (1981)

Sys. Hexagonal S.G. $P3_121$ (152)
a_0 4.9133(2) b_0 c_0 5.4053(4) A C 1.1001
α β γ Z 3 Dx 2.649
Ref. Ibid.

εα nωβ 1.544 εγ 1.553 Sign +
2V D 2.656 mp Color Colorless
Ref. Ibid.

Sample from the Glass Section at the National Bureau of Standards; ground single crystals of optical quality, locality unknown. Pattern at 25°C.
Silicon (a_0=5.43088Å) used as internal standard.
F_{30} = 76.6(0.0126,31). Quartz group.
To replace 5-490.

d A	I/I_1	hkl	d A	I/I_1	hkl
4.257	22	100	1.2285	1	220
3.342	100	101	1.1999	2	213
2.457	8	110	1.1978	1	221
2.282	8	102	1.1843	3	114
2.237	4	111	1.1804	3	310
2.127	6	200	1.1532	1	311
1.9792	4	201	1.1405	<1	204
1.8179	14	112	1.1143	<1	303
1.8021	<1	003	1.0813	2	312
1.6719	4	202	1.0635	<1	400
1.6591	2	103	1.0476	1	105
1.6082	<1	210	1.0438	<1	401
1.5418	9	211	1.0347	<1	214
1.4536	1	113	1.0150	1	223
1.4189	<1	300	0.9898	1	402
1.3820	6	212	.9873	1	313
1.3752	7	203	.9783	<1	304
1.3718	8	301	.9762	1	320
1.2880	2	104	.9636	<1	205
1.2558	2	302	6 reflections		to 0.9089

1-0378 MAJOR CORRECTION

d (0831 / 1-0363)	4.30	3.81	4.08	4.30	SiO_2 — Silicon di Oxide	SiO_2 — Tridymite (low form)
I/I_1 (1-0378)	100	67	33	100		

Rad. MoKα λ 0.709 Filter ZrO_2
Dia. 16 inches Cut off Coll.
I/I_1 Calibrated strips d corr. abs.? No
Ref. H_1

Sys. Orthorhombic S.G.
a_0 9.88 b_0 17.1 c_0 16.3 A 0.578 C 0.954
α β γ Z 64 ?
Ref. Wy (for only one type of Tridymite)

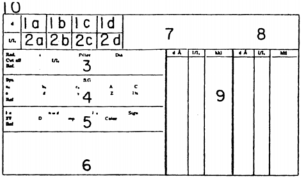
εα 1.478 nωβ 1.479 εγ 1.481 Sign +
2V 35° D 2.26 mp Color Colorless
Ref. Wn, C.C. (for only one type of Tridymite)

T.P. to β_1 (lower high-tridymite) at 117°C
T.P. to β_2 (upper high-tridymite) at 163°C
Specimen was Haws Refractory Brick
Low Tridymite occurs in many polytypic forms, the patterns of which are characterized by the same strong reflections and different weak ones (see also other Tridymite cards). See Florke, Ber. deut. keram. Ges. 32,369-82(1955) for reproductions of powder photographs.

d Å	I/I_1	hkl	d Å	I/I_1	hkl
4.30	100		1.44	3	
4.08	33		1.40	7	
3.81	67		1.36	3	
3.43	1		1.31	4	
3.21	1		1.25	3	
2.96	17		1.19	5	
2.80	3		1.15	3	
2.49	27		1.10	1	
2.31	11				
2.08	5				
1.84	3				
1.69	8				
1.64	4				
1.60	4				
1.53	5				

Phase analysis with the PDF database

EXPLANATION OF THE FORMAT



The card shown above has spaces numbered from 1 to 10 inclusive. The explanation of the symbols in the various spaces is as follows:

Spaces 1a, 1b and 1c

These contain the interplanar spacings corresponding to the three strongest lines in the diffraction pattern, chosen from the forward reflections, where $2\theta < 90°$. Note that where $2\theta = 90°$, the value of dA depends upon the wavelength of the radiation used.

Space 1d

This gives the largest interplanar spacing found for the specimen.

Spaces 2a, 2b, 2c and 2d

These contain the intensities of the lines in Spaces 1a, 1b, 1c, 1d, referred to the strongest line as 100. This intensity occasionally is given a number greater than 100 when it is very much stronger than the rest of the pattern.

Space 3

Rad.—Source of the x-rays (Mo, Cu, etc.)
λ—The wave length of the x-rays used in Angstroms.
Filter—The substance used to filter out extraneous wave lengths.
Dia.—The diameter of the cylindrical film holder.
Cut off—The longest spacing possible with the apparatus used.
I/I_1—The method used to measure relative intensities. This ordinarily means either diffractometer, calibrated strips of photographic film or visual inspection. The relative intensities are expressed on a scale 0—100 in steps of 10 for visually estimated values, and more exactly for measured values.
Ref.—Source of the data listed in Spaces 3 and 9.

Space 4

Sys.—Crystallographic system to which the specimen belongs.
S. G.—Space group, listed according to the Schoenflies system and the system given in "International Tables for X-ray Crystallography" (1952).
a_o, b_o, and c_o—Lattice parameters. $A = a_o/b_o$ $C = c_o/b_o$.
α, β, γ—Interaxial angles.
Z—The numbers of chemical formula units per unit of structure. For chemical elements, Z represents the number of atoms per unit of structure; for compounds, Z represents the number of formula units per unit cell. Spaces 7 and 8 show usually the simplest atomic formula for the compound. The "dot" formula has been multiplied by an appropriate factor to make it agree with the formula in Space 7.
Dx—Density calculated from x-ray measurements.
Ref.—Source of the data listed in Space 4.

Space 5

$\epsilon\alpha$, $n_\omega\beta$, and $\epsilon\gamma$—Indices of refraction.
Sign and 2V have the customary crystallographic meanings.
D—Measured density.
mp—Melting point.
Color—The color of the specimen as ordinarily seen or as seen when examined by microscopic methods. Occasionally other data are listed in this space, such as hardness (H) and luster of minerals.
Ref.—Source of the data listed in Space 5.

Space 6

This contains further pertinent information, such as chemical analysis of the specimen, source of the sample, heat treatment, temperature at which the pattern was made, etc.

Space 7

Chemical formula and name of the specimen. The formula may be omitted in cases of too complex compositions.

Space 8

"Dot" or structural formula for the specimen, when available, above the mineralogical or common name, if any, of the specimen. Parentheses around the name indicates a synthetic material. A ★ in the upper right corner of this space indicates that the card contains data of high reliability; a O indicates low reliability.

Space 9

This provides columns of interplanar spaces, relative intensities, and Miller indices.

The following abbreviations may be used in Space 9:

b = Broad, fuzzy or diffuse line
d = Doublet
n = Line not given by all sources
nc = Line not accounted for by the proposed unit cell
ni = Line cannot be indexed with given unit cell
np = Index not permitted by given space group
β = Intensity uncertain owing to presence of, or overlapping of, β lines
tr = Trace
\+ = Additional indices are possible

Space 10

The location of the identification number of the card. Because of changes in the d-spacings of many of the patterns in these sets, the identification number no longer shows the Hanawalt order of the card in the File and should be considered an arbitrary number only.

Phase analysis with the PDF database

Powder Diffraction File Search Manual

Hanawalt Method

Inorganic

1987

Published by the

INTERNATIONAL CENTRE FOR DIFFRACTION DATA

1601 PARK LANE • SWARTHMORE, PA 19081-2389 • U.S.A.

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	14.1_8	28.0_x	2.98_8	2.70_8	4.85_6	4.44_5	5.27_4	5.60_3	$CaCu_5(AsO_4)_2(CO_3)(OH)_4\cdot 6H_2O$/Tyrolite	11– 348
	8.04_x	24.1_x	3.44_x	3.02_x	2.68_8	1.61_8	1.78_7	2.41_6	$Na_4BaTi_2NbSi_4O_{17}(F,OH)\cdot Na_3PO_4$/Bornemanite	29–1176
	11.9_x	23.1_x	9.10_1	3.18_1	6.91_1	13.9_1	9.70_1	8.00_1	$Fe_4(PO_4)_3(OH)_3\cdot 12H_2O$/Cacoxenite	14– 331
i	11.0_8	22.0_x	3.12_x	4.20_8	1.82_8	3.65_6	2.80_6	8.40_4	$Ca_4(Si_6O_{15})(OH)_2\cdot 3H_2O$/Gyrolite	9– 449
o	11.7_8	21.0_x	4.12_x	1.40_x	7.80_8	3.75_8	2.32_8	5.70_4	$Al_4Si_3O_7(OH)_{10}\cdot xH_2O$/Imogolite	25–1493
i	8.84_8	21.0_x	1.82_7	2.95_6	2.92_6	3.11_6	3.00_6	2.80_5	$CaSi_2O_5\cdot 2H_2O$/Okenite	33– 305
	8.97_9	18.7_x	2.86_x	3.13_9	9.46_8	4.79_8	4.21_8	3.35_8	$Cu_8(AsO_4)_4(OH)_4\cdot 5H_2O$/Strashimirite	21– 289
i	9.23_x	18.4_x	5.57_7	6.15_6	3.58_6	3.49_6	4.20_4	5.32_3	$Fe_{14}O_3(SO_4)_{18}\cdot 63H_2O$/Copiapite	35– 583
i	9.08_x	18.2_8	2.02_4	3.29_3	2.90_2	3.76_2	3.07_2	2.60_2	$Na_6K_2Fe_7(SO_4)_{12}O_2\cdot 18H_2O$/Metavoltine	29–1043
	9.20_x	18.1_8	5.58_8	6.17_7	3.58_5	3.50_5	5.32_3	4.68_3	$(Mg,Al)(Fe,Al)_4(SO_4)_6(OH)_2\cdot 20H_2O$/Aluminocopi	20– 659
	8.94_x	17.7_9	2.84_8	5.57_6	2.96_6	2.68_6	1.71_5	3.85_4	$K_3Na_2Ca_{10}Al_{15}(PO_4)_{21}(OH)_7\cdot 26H_2O$/Englishite	29–1037
o	8.65_8	17.6_x	3.33_x	7.85_7	12.2_6	7.44_6	2.37_6	4.25_4	$(Al,Fe)_3AsO_4(OH)_6\cdot 5H_2O$/Liskeardite	11– 146
i	15.1_8	17.0_x	11.3_x	12.2_9	11.1_8	8.57_8	5.98_8	9.80_6	$Hf(OH)_2SO_4\cdot 2H_2O$	21– 361
i	12.2_9	17.0_x	11.3_x	15.1_8	11.1_8	8.57_8	5.98_8	9.80_6	$Hf(OH)_2SO_4\cdot 2H_2O$	21– 361

FINK POWDER DIFFRACTION FILE RETRIEVAL INDEX

for

INORGANIC COMPOUNDS

1972

Publication PD1S-22f

Published by the

JOINT COMMITTEE ON POWDER DIFFRACTION STANDARDS

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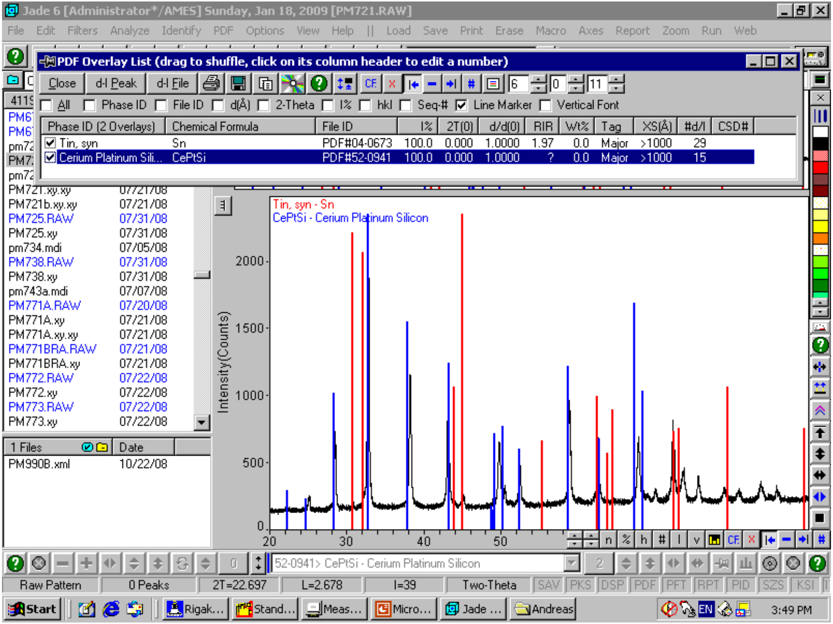
10.0 and over

										File No.	Fiche No.
	30.4_x	15.2_8	10.0_1	5.01_2	4.48_3	3.30_1	2.56_1	1.49_1	Al-Fe-Mg-Ca-Na-K-Si-O.H_2O	22- 956	I-153-F 3
*	17.0_x	15.1_8	12.2_9	11.3_x	11.1_8	9.80_6	8.57_8	5.98_8	$Hf(OH)_2SO_4.2H_2O$	21- 361	I-134-C 3
	30.0_6	15.0_9	4.97_8	4.53_x	3.29_3	2.98_3	2.54_5	1.51_5	Na-K-Ca-Mg-Al-Si-O-OH-H_2O	12- 231	I- 46-B 5
	29.2_5	14.6_x	9.70_1	7.30_3	4.90_4	3.63_4	3.27_1	2.92_2	$Mg_8Al_3Si_6O_{20}(OH)_{10}.4H_2O$	13- 190	I- 52-E 4
	28.0_x	14.1_8	5.60_3	5.27_4	4.85_6	4.44_5	2.98_8	2.70_8	$Ca_2Cu_9(AsO_4)_4(OH)_{10}.10H_2O$	11- 348	I- 40-F 7
	29.0_3	14.0_x	7.08_6	4.72_3	4.62_3	3.53_6	2.83_3	2.57_3	MgFeAlSi	19- 764	I-109-F 1
*	23.1_x	13.9_1	11.9_x	9.70_1	9.10_1	8.00_1	6.91_1	3.18_1	$Fe_4(PO_4)_3(OH)_3.12H_2O$	14- 331	I- 59-B 6
*	16.1_4	13.8_4	10.6_5	9.07_5	7.12_x	4.82_7	4.72_6	3.83_2	$C_2H_8N_2O_8U.3H_2O$	19- 69	I-103-E 2
o	14.5_x	12.9_1	11.8_1	7.20_1	4.88_1	4.25_1	2.60_1	0.00_1	$NaGa_5O_8$	21-1114	I-141-B 3
	25.8_x	12.4_8	4.95_4	4.47_8	4.30_4	3.33_5	2.56_5	1.49_5	Al-Ti-Fe-K-Na-Si-OH	7- 330	I- 26-C 3
	25.5_x	12.4_x	8.20_3	6.15_1	4.92_6	4.11_2	3.53_x	3.09_x	K-Mg-Fe-Al-Si-O-OH	13- 233	I- 53-B 3
	24.7_x	12.4_5	4.94_1	3.54_1	3.10_2	2.48_1	2.05_1	1.90_1	Na-Ca-K-H_3O-Al-Si-O-H.$3H_2O$	14- 183	I- 57-E12
o	17.6_x	12.2_6	8.65_8	7.85_7	7.44_6	4.25_4	3.33_x	2.37_6	$(Al,Fe)_3AsO_4(OH)_6.5H_2O$	11- 146	I- 39-B11
*	15.1_8	12.2_9	11.3_x	11.1_8	9.80_6	8.57_8	5.98_8	17.0_x	$Hf(OH)_2SO_4.2H_2O$	21- 361	I-134-C 3
	17.4_3	12.1_x	10.6_6	5.79_4	4.35_4	3.53_3	2.90_5	2.12_5	$V_2O_5.3H_2O$	7- 332	I- 26-C 4

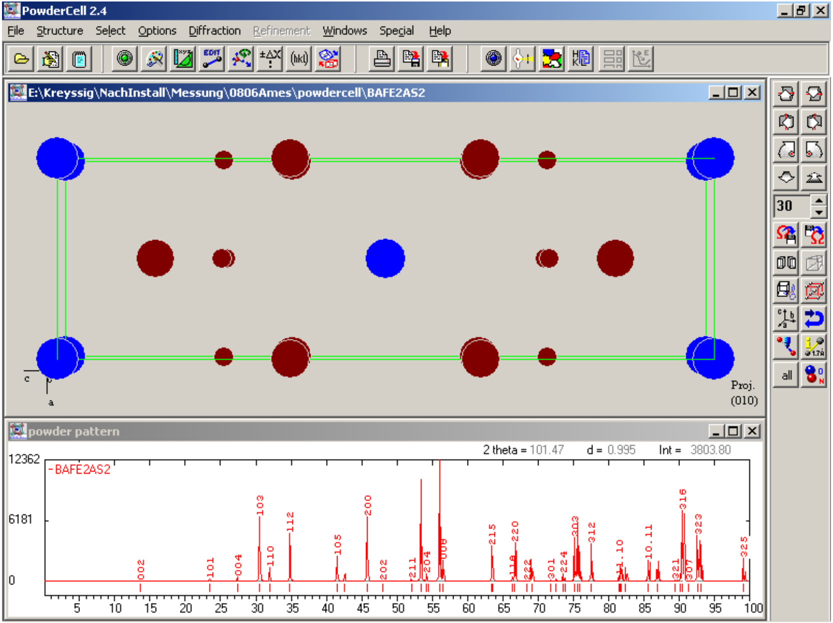
Example: growth of PrAuSi out of Sn flux



If your phase is not in the database – search for isostructural compounds...

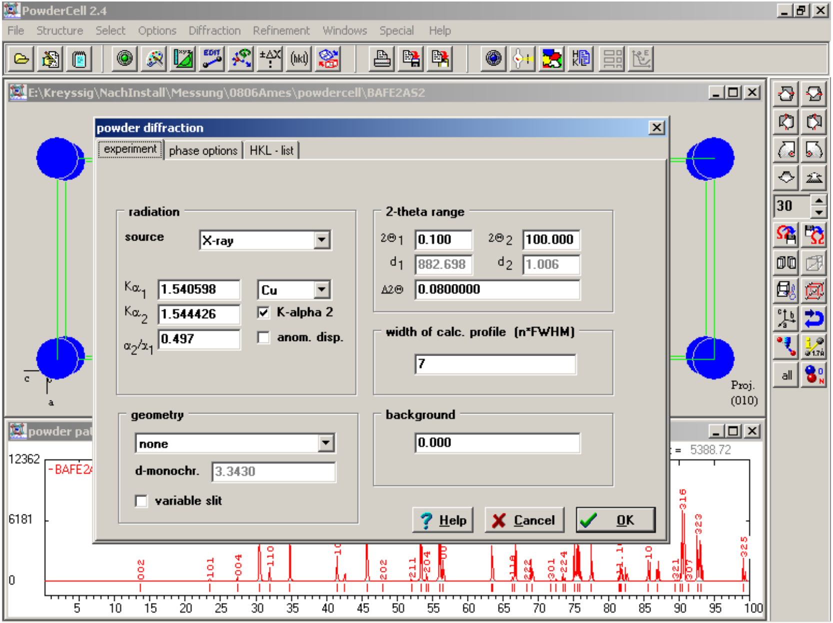
E. D. Mun: PM721-Ex1g

Powdercell



The best tool to calculate diffraction pattern, to verify structure data and more…

Powdercell



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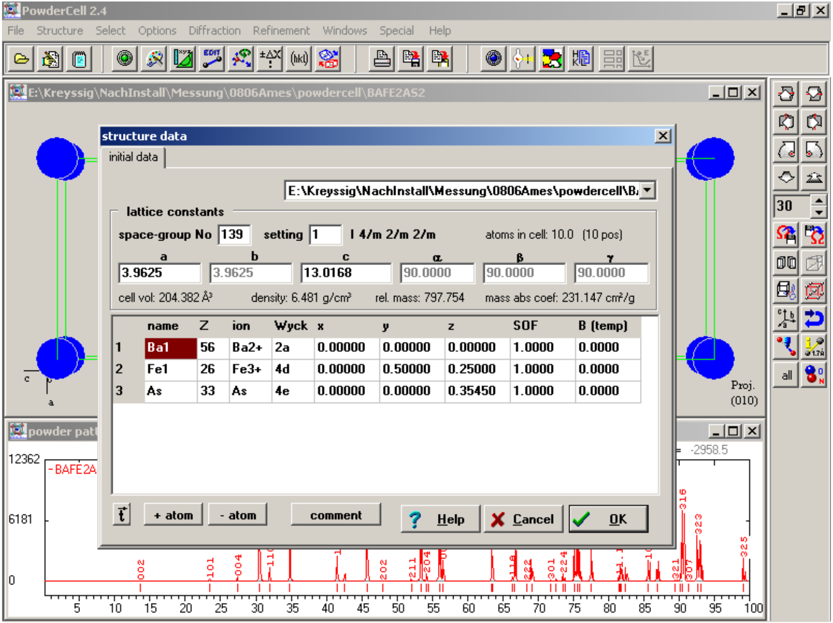


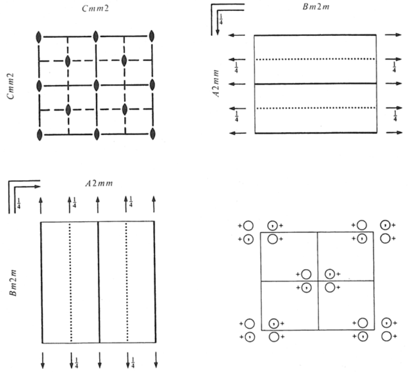
The best tool to calculate diffraction pattern, to verify structure data and more…

International Tables for Crystallography

① $Cmm2$ $\quad C_{2v}^{11}$ $\quad mm2$ $\quad$ Orthorhombic

② No. 35 $\quad Cmm2$ $\quad$ Patterson symmetry $Cmmm$

③



④ **Origin** on $mm2$

⑤ **Asymmetric unit** $\quad 0 \le x \le \frac{1}{4}; \quad 0 \le y \le \frac{1}{2}; \quad 0 \le z \le 1$

⑥ **Symmetry operations**

For $(0,0,0)+$ set

(1) 1	(2) $2 \quad 0,0,z$	(3) $m \quad x,0,z$	(4) $m \quad 0,y,z$

For $(\frac{1}{2},\frac{1}{2},0)+$ set

(1) $t(\frac{1}{2},\frac{1}{2},0)$	(2) $2 \quad \frac{1}{4},\frac{1}{4},z$	(3) $a \quad x,\frac{1}{4},z$	(4) $b \quad \frac{1}{4},y,z$

International Tables for Crystallography

①	*Headline*: Section 2.2.3. Short Hermann–Mauguin symbol (Section 2.2.4 and Chapter 12.2)	Schoenflies symbol (Chapters 12.1 and 12.2)	Crystal class (Point group) (Section 10.1.1 and Chapter 12.1)	Crystal system (Section 2.1.2)
②	Number of space group [Same as in *IT* (1952)]	Full Hermann–Mauguin symbol (Section 2.2.4 and Chapter 12.3)		Patterson symmetry (Section 2.2.5)

③ *Space-group diagrams*, consisting of one or several projections of the symmetry elements and one illustration of a set of equivalent points in general position. The numbers and types of the diagrams depend on the crystal system. The diagrams and their axes are described in Section 2.2.6; the graphical symbols of symmetry elements are listed in Chapter 1.4.

For monoclinic space groups see Section 2.2.16; for orthorhombic settings see Section 2.2.6.4.

④ *Origin* of the unit cell: Section 2.2.7. The site symmetry of the origin and its location with respect to the symmetry elements are given.

⑤ *Asymmetric unit*: Section 2.2.8. One choice of asymmetric unit is given.

⑥ *Symmetry operations*: Section 2.2.9 and Part 11. For each point $\tilde{x}, \tilde{y}, \tilde{z}$ of the general position that symmetry operation is listed which transforms the initial point x, y, z into the point under consideration. The symbol describes the nature of the operation, its glide or screw component (given between parentheses), if present, and the location of the corresponding symmetry element.

The symmetry operations are numbered in the same way as the corresponding coordinate triplets of the general position. For centred space groups the same numbering is applied in each block, *e.g.* under 'For $(\frac{1}{2}, \frac{1}{2}, 0)+$ set'.

[*Continued on inside back cover*]

International Tables for Crystallography

1.4.1. Symmetry planes normal to the plane of projection (three dimensions) and symmetry lines in the plane of the figure (two dimensions)

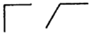
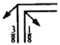
Symmetry plane or symmetry line	Graphical symbol	Glide vector in units of lattice translation vectors parallel and normal to the projection plane	Printed symbol
Reflection plane, mirror plane Reflection line, mirror line (two dimensions)		None	*m*
'Axial' glide plane Glide line (two dimensions)		$\frac{1}{2}$ lattice vector along line in projection plane $\frac{1}{2}$ lattice vector along line in plane	*a*, *b* or *c* *g*
'Axial' glide plane		$\frac{1}{2}$ lattice vector normal to projection plane	*a*, *b* or *c*
'Double' glide plane* (in centred cells only)		*Two* glide vectors: $\frac{1}{2}$ along line parallel to projection plane, $\frac{1}{2}$ normal to projection plane	*e*
'Diagonal' glide plane		*One* glide vector with *two* components: $\frac{1}{2}$ along line parallel to projection plane, $\frac{1}{2}$ normal to projection plane	*n*
'Diamond' glide plane† (pair of planes; in centred cells only)		$\frac{1}{4}$ along line parallel to projection plane, combined with $\frac{1}{4}$ normal to projection plane (arrow indicates direction parallel to the projection plane for which the normal component is positive)	*d*

* For further explanations of the 'double' glide plane *e* see Note (iv) below and Note (x) in Chapter 1.3.

† See footnote § to Section 1.3.1.

International Tables for Crystallography

1.4.2. Symmetry planes parallel to the plane of projection

Symmetry plane	Graphical symbol*	Glide vector in units of lattice translation vectors parallel to the projection plane	Printed symbol
Reflection plane, mirror plane		None	*m*
'Axial' glide plane		$\frac{1}{2}$ lattice vector in the direction of the arrow	*a*, *b* or *c*
'Double' glide plane† (in centred cells only)		*Two* glide vectors: $\frac{1}{2}$ in either of the directions of the two arrows	*e*
'Diagonal' glide plane		*One* glide vector with *two* components $\frac{1}{2}$ in the direction of the arrow	*n*
'Diamond' glide plane‡ (pair of planes; in centred cells only)		$\frac{1}{2}$ in the direction of the arrow; the glide vector is always half of a centring vector, *i.e.* one quarter of a diagonal of the conventional face-centred cell	*d*

* The symbols are given at the upper left corner of the space-group diagrams. A fraction h attached to a symbol indicates two symmetry planes with 'heights' h and $h+\frac{1}{2}$ above the plane of projection; *e.g.* $\frac{1}{8}$ stands for $h=\frac{1}{8}$ and $\frac{5}{8}$. No fraction means $h=0$ and $\frac{1}{2}$ (*cf.* Section 2.2.6).

† For further explanations of the 'double' glide plane *e* see Note (iv) below and Note (x) in Chapter 1.3.

‡ See footnote § to Section 1.3.1.

International Tables for Crystallography

1.4.5. Symmetry axes normal to the plane of projection and symmetry points in the plane of the figure

Symmetry axis or symmetry point	Graphical symbol*	Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed symbol (partial elements in parentheses)
Identity	None	None	1
Twofold rotation axis Twofold rotation point (two dimensions)		None	2
Twofold screw axis: '2 sub 1'		$\frac{1}{2}$	2_1
Threefold rotation axis Threefold rotation point (two dimensions)		None	3
Threefold screw axis: '3 sub 1'		$\frac{1}{3}$	3_1
Threefold screw axis: '3 sub 2'		$\frac{2}{3}$	3_2
Fourfold rotation axis Fourfold rotation point (two dimensions)		None	4 (2)
Fourfold screw axis: '4 sub 1'		$\frac{1}{4}$	4_1 (2_1)
Fourfold screw axis: '4 sub 2'		$\frac{1}{2}$	4_2 (2)
Fourfold screw axis: '4 sub 3'		$\frac{3}{4}$	4_3 (2_1)
Sixfold rotation axis Sixfold rotation point (two dimensions)		None	6 (3,2)
Sixfold screw axis: '6 sub 1'		$\frac{1}{6}$	6_1 $(3_1, 2_1)$
Sixfold screw axis: '6 sub 2'		$\frac{1}{3}$	6_2 $(3_2, 2)$
Sixfold screw axis: '6 sub 3'		$\frac{1}{2}$	6_3 $(3, 2_1)$
Sixfold screw axis: '6 sub 4'		$\frac{2}{3}$	6_4 $(3_1, 2)$
Sixfold screw axis: '6 sub 5'		$\frac{5}{6}$	6_5 $(3_2, 2_1)$
Centre of symmetry, inversion centre: '1 bar' Reflection point, mirror point (one dimension)		None	$\bar{1}$
Inversion axis: '3 bar'		None	$\bar{3}$ $(3, \bar{1})$
Inversion axis: '4 bar'		None	$\bar{4}$ (2)
Inversion axis: '6 bar'		None	$\bar{6} \equiv 3/m$
Twofold rotation axis with centre of symmetry		None	$2/m$ $(\bar{1})$
Twofold screw axis with centre of symmetry		$\frac{1}{2}$	$2_1/m$ $(\bar{1})$
Fourfold rotation axis with centre of symmetry		None	$4/m$ $(\bar{4}, 2, \bar{1})$
'4 sub 2' screw axis with centre of symmetry		$\frac{1}{2}$	$4_2/m$ $(\bar{4}, 2, \bar{1})$
Sixfold rotation axis with centre of symmetry		None	$6/m$ $(\bar{6}, \bar{3}, 3, 2, \bar{1})$
'6 sub 3' screw axis with centre of symmetry		$\frac{1}{2}$	$6_3/m$ $(\bar{6}, \bar{3}, 3, 2_1, \bar{1})$

* Notes on the 'heights' h of symmetry points $\bar{1}$, $\bar{3}$, $\bar{4}$ and $\bar{6}$:

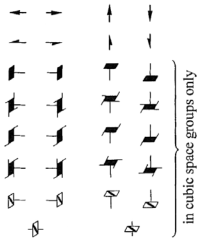
(1) Centres of symmetry $\bar{1}$ and $\bar{3}$, as well as inversion points $\bar{4}$ and $\bar{6}$ on $\bar{4}$ and $\bar{6}$ axes parallel to [001], occur in pairs at 'heights' h and $h+\frac{1}{2}$. In the space-group diagrams, only one fraction h is given, *e.g.* $\frac{1}{4}$ stands for $h=\frac{1}{4}$ and $\frac{3}{4}$. No fraction means $h=0$ and $\frac{1}{2}$. In *cubic* space groups, however, *both* fractions are given for vertical $\bar{4}$ axes, including $h=0$ and $\frac{1}{2}$.

(2) Symmetries $4/m$ and $6/m$ contain vertical $\bar{4}$ and $\bar{6}$ axes; their $\bar{4}$ and $\bar{6}$ inversion points coincide with the centres of symmetry. This is not indicated in the space-group diagrams.

(3) Symmetries $4_2/m$ and $6_3/m$ also contain vertical $\bar{4}$ and $\bar{6}$ axes, but their $\bar{4}$ and $\bar{6}$ inversion points alternate with the centres of symmetry; *i.e.* $\bar{1}$ points at h and $h+\frac{1}{2}$ interleave with $\bar{4}$ or $\bar{6}$ points at $h+\frac{1}{4}$ and $h+\frac{3}{4}$. In the tetragonal and hexagonal space-group diagrams, only *one* fraction for $\bar{1}$ and one for $\bar{4}$ or $\bar{6}$ is given. In the cubic diagrams, *all four* fractions are listed for $4_2/m$; *e.g.* $Pm\bar{3}n$ (No. 223): $\bar{1}$: 0, $\frac{1}{2}$; $\bar{4}$: $\frac{1}{4}$, $\frac{3}{4}$.

International Tables for Crystallography

1.4.6. Symmetry axes parallel to the plane of projection

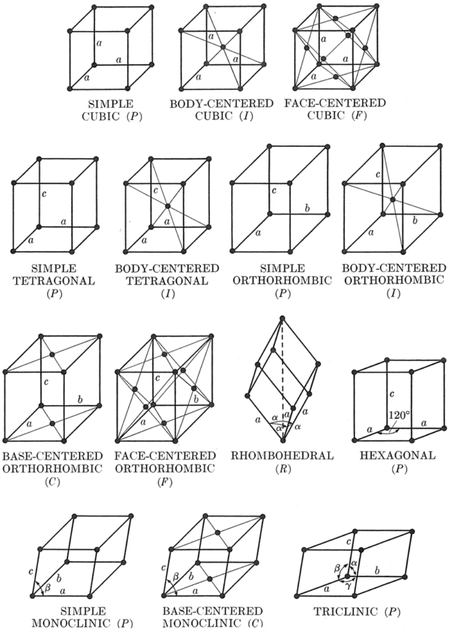
Symmetry axis	Graphical symbol*	Screw vector of a right-handed screw rotation in units of the shortest lattice translation vector parallel to the axis	Printed symbol (partial elements in parentheses)
Twofold rotation axis		None	2
Twofold screw axis: '2 sub 1'		$\frac{1}{2}$	2_1
Fourfold rotation axis		None	4 (2)
Fourfold screw axis: '4 sub 1'		$\frac{1}{4}$	4_1 (2_1)
Fourfold screw axis: '4 sub 2'		$\frac{1}{2}$	4_2 (2)
Fourfold screw axis: '4 sub 3'		$\frac{3}{4}$	4_3 (2_1)
Inversion axis: '4 bar'		None	$\bar{4}$ (2)
Inversion point on '4 bar'-axis		–	$\bar{4}$ point

* The symbols for horizontal symmetry axes are given outside the unit cell of the space-group diagrams. *Twofold* axes always occur in pairs, at 'heights' h and $h+\frac{1}{2}$ above the plane of projection; here, a fraction h attached to such a symbol indicates two axes with heights h and $h+\frac{1}{2}$. No fraction stands for $h=0$ and $\frac{1}{2}$. The rule of pairwise occurrence is not valid for the horizontal *fourfold* axes in cubic space groups; here, *all* heights are given, including $h=0$ and $\frac{1}{2}$. This applies also to the horizontal $\bar{4}$ axes and the $\bar{4}$ inversion points located on these axes.

International Tables for Crystallography

System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \quad \alpha = \beta = \gamma = 90°$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c, \quad \alpha = \beta = \gamma \neq 90°$	Simple	R
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c, \quad \alpha = \beta = 90°, \quad \gamma = 120°$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \quad \alpha = \gamma = 90° \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \quad \alpha \neq \beta \neq \gamma \neq 90°$	Simple	P

* Also called trigonal.



Cullity 35, 36

International Tables for Crystallography

② **Generators selected** (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},0)$; (2); (3)

③ **Positions**

Multiplicity, Wyckoff letter, Site symmetry			Coordinates $(0,0,0)+\ (\frac{1}{2},\frac{1}{2},0)+$				Reflection conditions
							General:
8	f	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $x,\bar{y},z$	(4) $\bar{x},y,z$	$hkl: h+k=2n$ $0kl: k=2n$ $h0l: h=2n$ $hk0: h+k=2n$ $h00: h=2n$ $0k0: k=2n$
							Special: as above, plus
4	e	$m..$	$0,y,z$	$0,\bar{y},z$			no extra conditions
4	d	$.m.$	$x,0,z$	$\bar{x},0,z$			no extra conditions
4	c	$..2$	$\frac{1}{4},\frac{1}{4},z$	$\frac{1}{4},\frac{3}{4},z$			$hkl: h=2n$
2	b	$mm2$	$0,\frac{1}{2},z$				no extra conditions
2	a	$mm2$	$0,0,z$				no extra conditions

④ **Symmetry of special projections**

Along [001] $c2mm$
$\mathbf{a}'=\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$
Origin at $0,0,z$

Along [100] $p1m1$
$\mathbf{a}'=\frac{1}{2}\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$
Origin at $x,0,0$

Along [010] $p11m$
$\mathbf{a}'=\mathbf{c}$ $\mathbf{b}'=\frac{1}{2}\mathbf{a}$
Origin at $0,y,0$

⑤ **Maximal non-isomorphic subgroups**

I [2] $C1m1$ (Cm, 8) (1; 3)+
[2] $Cm11$ (Cm, 8) (1; 4)+
[2] $C112$ ($P2$, 3) (1; 2)+

IIa [2] $Pba2$ (32) 1; 2; (3; 4) + $(\frac{1}{2},\frac{1}{2},0)$
[2] $Pbm2$ ($Pma2$, 28) 1; 3; (2; 4) + $(\frac{1}{2},\frac{1}{2},0)$
[2] $Pma2$ (28) 1; 4; (2; 3) + $(\frac{1}{2},\frac{1}{2},0)$
[2] $Pmm2$ (25) 1; 2; 3; 4

IIb [2] $Ima2$ ($\mathbf{c}'=2\mathbf{c}$) (46); [2] $Ibm2$ ($\mathbf{c}'=2\mathbf{c}$) ($Ima2$, 46); [2] $Iba2$ ($\mathbf{c}'=2\mathbf{c}$) (45); [2] $Imm2$ ($\mathbf{c}'=2\mathbf{c}$) (44); [2] $Ccc2$ ($\mathbf{c}'=2\mathbf{c}$) (37); [2] $Cmc2_1$ ($\mathbf{c}'=2\mathbf{c}$) (36); [2] $Ccm2_1$ ($\mathbf{c}'=2\mathbf{c}$) ($Cmc2_1$, 36)

⑥ **Maximal isomorphic subgroups of lowest index**

IIc [2] $Cmm2$ ($\mathbf{c}'=2\mathbf{c}$) (35); [3] $Cmm2$ ($\mathbf{a}'=3\mathbf{a}$ or $\mathbf{b}'=3\mathbf{b}$) (35)

⑦ **Minimal non-isomorphic supergroups**

I [2] $Cmmm$ (65); [2] $Cmme$ (67); [2] $P4mm$ (99); [2] $P4bm$ (100); [2] $P4_2cm$ (101); [2] $P4_2nm$ (102); [2] $P\bar{4}2m$ (111); [2] $P\bar{4}2_1m$ (113); [3] $P6mm$ (183)

II [2] $Fmm2$ (42); [2] $Pmm2$ ($\mathbf{a}'=\frac{1}{2}\mathbf{a},\mathbf{b}'=\frac{1}{2}\mathbf{b}$) (25)

International Tables for Crystallography

① *Headline* in abbreviated form.

② *Generators selected*: Sections 2.2.10 and 8.3.5. A set of generators, as selected for these *Tables*, is listed in the form of translations and numbers of general-position coordinates. The generators determine the sequence of the coordinate triplets in the general position and of the corresponding symmetry operations.

③ *Positions*: Sections 2.2.11 and 8.3.2. The general Wyckoff position is given at the top, followed downwards by the various special Wyckoff positions with decreasing multiplicity and increasing site symmetry. For each general and special position its multiplicity, Wyckoff letter, oriented site-symmetry symbol, as well as the appropriate coordinate triplets and the reflection conditions, are listed. The coordinate triplets of the general position are numbered sequentially; *cf. Symmetry operations*.

Oriented site-symmetry symbol (third column): Section 2.2.12. The site symmetry at the points of a special position is given in oriented form.

Reflection conditions (right-most column): Section 2.2.13.

[*Lattice complexes* are described in Part 14; Tables 14.2.3.1 and 14.2.3.2 show the assignment of Wyckoff positions to Wyckoff sets and to lattice complexes.]

④ *Symmetry of special projections*: Section 2.2.14. For each space group, orthographic projections along three (symmetry) directions are listed. Given are the projection direction, the plane group of the projection, as well as the axes and the origin of the projected cell.

⑤ *Maximal non-isomorphic subgroups*: Sections 2.2.15 and 8.3.3.

Type **I**: *translationengleiche* or *t* subgroups;
Type **IIa**: *klassengleiche* or *k* subgroups, obtained by 'decentring' the conventional cell; applies only to space groups with centred cells;
Type **IIb**: *klassengleiche* or *k* subgroups, obtained by enlarging the conventional cell.

Given are:
For types **I** and **IIa**: Index [between brackets]; 'unconventional' Hermann–Mauguin symbol of the subgroup; 'conventional' Hermann–Mauguin symbol of the subgroup, if different (between parentheses); coordinate triplets retained in subgroup.
For type **IIb**: Index [between brackets]; 'unconventional' Hermann–Mauguin symbol of the subgroup; basis-vector relations between group and subgroup (between parentheses); 'conventional' Hermann–Mauguin symbol of the subgroup, if different (between parentheses).

⑥ *Maximal isomorphic subgroups of lowest index*: Sections 2.2.15, 8.3.3 and 13.1.2.

Type **IIc**: *klassengleiche* or *k* subgroups of lowest index which are of the same type as the group, *i.e.* have the same standard Hermann–Mauguin symbol. Data as for subgroups of type **IIb**.

⑦ *Minimal non-isomorphic supergroups*: Sections 2.2.15 and 8.3.3.
The list contains the reverse relations of the subgroup tables; only types **I** (*t* supergroups) and **II** (*k* supergroups) are distinguished. Data as for subgroups of type **IIb**.

Problems describing a structure – Rhombohedral unit cell

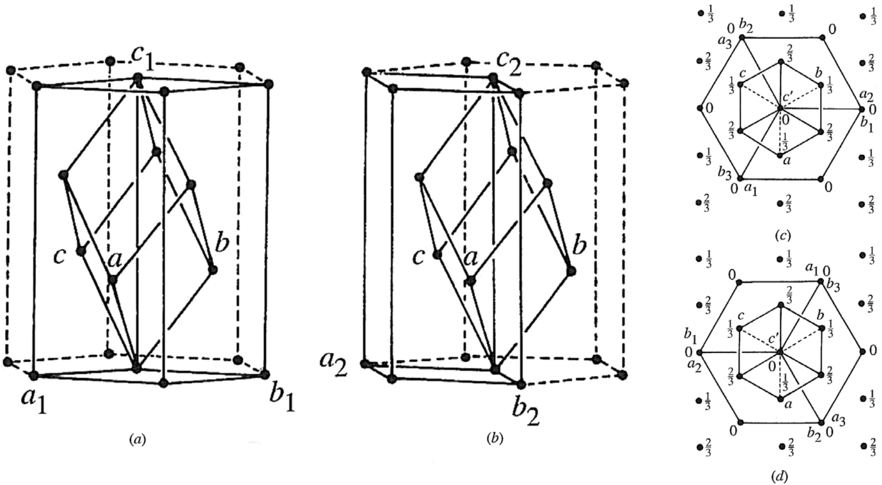


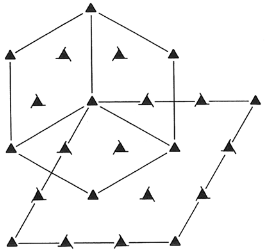
Fig. 5.1.3.6. Unit cells in the rhombohedral lattice: same origin for all cells. The basis of the rhombohedral cell is labelled a, b, c. Two settings of the triple hexagonal cell are possible with respect to a primitive rhombohedral cell: The *obverse setting* with the lattice points $0, 0, 0; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ has been used in *International Tables* since 1952. Its general reflection condition is $-h+k+l=3n$. The *reverse setting* with lattice points $0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{3}; \frac{2}{3}, \frac{1}{3}, \frac{2}{3}$ was used in the 1935 edition. Its general reflection condition is $h-k+l=3n$. (*a*) Obverse setting of triple hexagonal cell a_1, b_1, c_1 in relation to the primitive rhombohedral cell a, b, c. (*b*) Reverse setting of triple hexagonal cell a_2, b_2, c_2 in relation to the primitive rhombohedral cell a, b, c. (*c*) Primitive rhombohedral cell (--- lower edges), a, b, c in relation to the three triple hexagonal cells in obverse setting a_1, b_1, c'; a_2, b_2, c'; a_3, b_3, c'. Projection along c'. (*d*) Primitive rhombohedral cell (- - - lower edges), a, b, c in relation to the three triple hexagonal cells in reverse setting a_1, b_1, c'; a_2, b_2, c'; a_3, b_3, c'. Projection along c'.

Problems describing a structure – Rhombohedral unit cell

$R3$ $\qquad C_3^4 \qquad$ 3

No. 146 $\qquad R3$

HEXAGONAL AXES



Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{2}{3},\frac{1}{3},\frac{1}{3})$; (2)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		
			$(0,0,0)+$	$(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$	$(\frac{1}{3},\frac{2}{3},\frac{2}{3})+$
9	b	1	(1) x,y,z	(2) $\bar{y},x-y,z$	(3) $\bar{x}+y,\bar{x},z$
3	a	3 .	$0,0,z$		

Symmetry of special projections

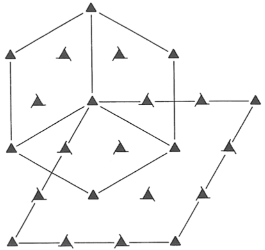
Along [001] $p3$
$\mathbf{a}' = \frac{1}{3}(2\mathbf{a}+\mathbf{b})$ $\quad \mathbf{b}' = \frac{1}{3}(-\mathbf{a}+\mathbf{b})$
Origin at $0,0,z$

Along [100] $p1$
$\mathbf{a}' = \frac{1}{2}(\mathbf{a}+2\mathbf{b})$ $\quad \mathbf{b}' = \frac{1}{3}(-\mathbf{a}-2\mathbf{b}+\mathbf{c})$
Origin at $x,0,0$

$R3$ $\qquad C_3^4 \qquad$ 3

No. 146 $\qquad R3$

RHOMBOHEDRAL AXES



Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		
3	b	1	(1) x,y,z	(2) z,x,y	(3) y,z,x
1	a	3 .	x,x,x		

Symmetry of special projections

Along [111] $p3$
$\mathbf{a}' = \frac{1}{3}(2\mathbf{a}-\mathbf{b}-\mathbf{c})$ $\quad \mathbf{b}' = \frac{1}{3}(-\mathbf{a}+2\mathbf{b}-\mathbf{c})$
Origin at x,x,x

Along [$1\bar{1}0$] $p1$
$\mathbf{a}' = \frac{1}{2}(\mathbf{a}+\mathbf{b}-2\mathbf{c})$ $\quad \mathbf{b}' = \mathbf{c}$
Origin at $x,\bar{x},0$

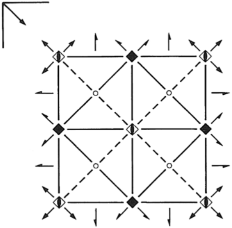
InternationalTables 146_11; 12a; 21; 22

Problems describing a structure – Origin of cell

$P4/nmm$ D_{4h}^{7}

No. 129 $P\ 4/n\ 2_1/m\ 2/m$

ORIGIN CHOICE 1



Origin at $\bar{4}m2$ at $\bar{4}/nm2/g$, at $-\frac{1}{4},\frac{1}{4},0$ from centre $(2/m)$

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le \frac{1}{2}$; $y \le \frac{1}{2} - x$

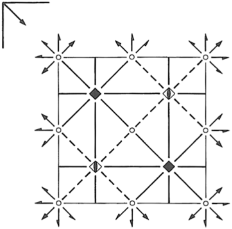
Symmetry operations

(1) 1	(2) $2\quad 0,0,z$	(3) $4^{+}\quad 0,\frac{1}{2},z$
(5) $2(0,\frac{1}{2},0)\quad \frac{1}{4},y,0$	(6) $2(\frac{1}{2},0,0)\quad x,\frac{1}{4},0$	(7) $2\quad x,x,0$
(9) $\bar{1}\quad \frac{1}{4},\frac{1}{4},0$	(10) $n(\frac{1}{2},\frac{1}{2},0)\quad x,y,0$	(11) $\bar{4}^{+}\quad 0,0,z;\ 0,0,0$
(13) $m\quad x,0,z$	(14) $m\quad 0,y,z$	(15) $m\quad x+\frac{1}{2},\bar{x},z$

$P4/nmm$ D_{4h}^{7}

No. 129 $P\ 4/n\ 2_1/m\ 2/m$

ORIGIN CHOICE 2



Origin at centre $(2/m)$ at $n2_1$ $(2/m,2_1/g)$, at $\frac{1}{4},-\frac{1}{4},0$ from $\bar{4}m2$

Asymmetric unit $-\frac{1}{4} \le x \le \frac{1}{4}$; $-\frac{1}{4} \le y \le \frac{1}{4}$; $0 \le z \le \frac{1}{2}$; $x \le y$

Symmetry operations

(1) 1	(2) $2\quad \frac{1}{4},\frac{1}{4},z$	(3) $4^{+}\quad \frac{1}{4},\frac{1}{4},z$
(5) $2(0,\frac{1}{2},0)\quad 0,y,0$	(6) $2(\frac{1}{2},0,0)\quad x,0,0$	(7) $2(\frac{1}{2},\frac{1}{2},0)\quad x,x,0$
(9) $\bar{1}\quad 0,0,0$	(10) $n(\frac{1}{2},\frac{1}{2},0)\quad x,y,0$	(11) $\bar{4}^{+}\quad \frac{1}{4},-\frac{1}{4},z;\ \frac{1}{4},-\frac{1}{4},0$
(13) $m\quad x,\frac{1}{4},z$	(14) $m\quad \frac{1}{4},y,z$	(15) $m\quad x+\frac{1}{2},\bar{x},z$

Problems describing a structure – Origin of cell

$P4/nmm$ $\quad D_{4h}^{7}$

No. 129 $\quad P\ 4/n\ 2_1/m\ 2/m$

ORIGIN CHOICE 1

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
16	k	1	(1) x,y,z	(2) $\bar{x},\bar{y},z$	(3) $\bar{y}+\frac{1}{2},x+\frac{1}{2},z$	
			(5) $\bar{x}+\frac{1}{2},y+\frac{1}{2},\bar{z}$	(6) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	(7) $y,x,\bar{z}$	
			(9) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	(10) $x+\frac{1}{2},y+\frac{1}{2},\bar{z}$	(11) $y,\bar{x},\bar{z}$	
			(13) $x,\bar{y},z$	(14) $\bar{x},y,z$	(15) $\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2},z$	
8	j	$..m$	$x,x+\frac{1}{2},z$	$\bar{x},\bar{x}+\frac{1}{2},z$	$\bar{x},x+\frac{1}{2},z$	$x,\bar{x}+\frac{1}{2},z$
			$\bar{x}+\frac{1}{2},x,\bar{z}$	$x+\frac{1}{2},\bar{x},\bar{z}$	$x+\frac{1}{2},x,\bar{z}$	$\bar{x}+\frac{1}{2},\bar{x},\bar{z}$
8	i	$.m.$	$0,y,z$	$0,\bar{y},z$	$\bar{y}+\frac{1}{2},\frac{1}{2},z$	$y+\frac{1}{2},\frac{1}{2},z$
			$\frac{1}{2},y+\frac{1}{2},\bar{z}$	$\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$	$y,0,\bar{z}$	$\bar{y},0,\bar{z}$
8	h	$..2$	$x,x,\frac{1}{2}$	$\bar{x},\bar{x},\frac{1}{2}$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},\frac{1}{2}$	
			$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},\frac{1}{2}$	$x+\frac{1}{2},x+\frac{1}{2},\frac{1}{2}$	$x,\bar{x},\frac{1}{2}$	
8	g	$..2$	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},0$	
			$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},0$	$x+\frac{1}{2},x+\frac{1}{2},0$	$x,\bar{x},0$	
4	f	$2mm.$	$0,0,z$	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$	$0,0,\bar{z}$
4	e	$..2/m$	$\frac{1}{4},\frac{1}{4},\frac{1}{2}$	$\frac{3}{4},\frac{3}{4},\frac{1}{2}$	$\frac{1}{4},\frac{3}{4},\frac{1}{2}$	$\frac{3}{4},\frac{1}{4},\frac{1}{2}$
4	d	$..2/m$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{3}{4},0$	$\frac{1}{4},\frac{3}{4},0$	$\frac{3}{4},\frac{1}{4},0$
2	c	$4mm$	$0,\frac{1}{2},z$	$\frac{1}{2},0,\bar{z}$		
2	b	$\bar{4}m2$	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
2	a	$\bar{4}m2$	$0,0,0$	$\frac{1}{2},\frac{1}{2},0$		

$P4/nmm$ $\quad D_{4h}^{7}$

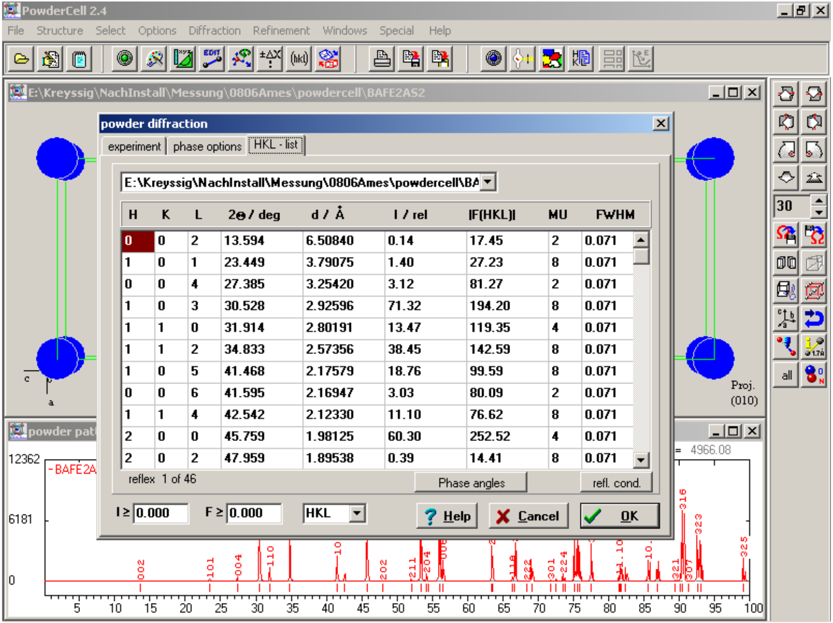
No. 129 $\quad P\ 4/n\ 2_1/m\ 2/m$

ORIGIN CHOICE 2

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates			
16	k	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y}+\frac{1}{2},z$	(3) $\bar{y}+\frac{1}{2},x,z$	
			(5) $\bar{x},y+\frac{1}{2},\bar{z}$	(6) $x+\frac{1}{2},\bar{y},\bar{z}$	(7) $y+\frac{1}{2},x+\frac{1}{2},\bar{z}$	
			(9) $\bar{x},\bar{y},\bar{z}$	(10) $x+\frac{1}{2},y+\frac{1}{2},\bar{z}$	(11) $y+\frac{1}{2},\bar{x},\bar{z}$	
			(13) $x,\bar{y}+\frac{1}{2},z$	(14) $\bar{x}+\frac{1}{2},y,z$	(15) $\bar{y}+\frac{1}{2},\bar{x}+\frac{1}{2},z$	
8	j	$..m$	x,x,z	$\bar{x}+\frac{1}{2},\bar{x}+\frac{1}{2},z$	$\bar{x}+\frac{1}{2},x,z$	$x,\bar{x}+\frac{1}{2},z$
			$\bar{x},x+\frac{1}{2},\bar{z}$	$x+\frac{1}{2},\bar{x},\bar{z}$	$x+\frac{1}{2},x+\frac{1}{2},\bar{z}$	$\bar{x},\bar{x},\bar{z}$
8	i	$.m.$	$\frac{1}{4},y,z$	$\frac{1}{4},\bar{y}+\frac{1}{2},z$	$\bar{y}+\frac{1}{2},\frac{1}{4},z$	$y,\frac{1}{4},z$
			$\frac{3}{4},y+\frac{1}{2},\bar{z}$	$\frac{3}{4},\bar{y},\bar{z}$	$y+\frac{1}{2},\frac{3}{4},\bar{z}$	$\bar{y},\frac{3}{4},\bar{z}$
8	h	$..2$	$x,\bar{x},\frac{1}{2}$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},\frac{1}{2}$	$x+\frac{1}{2},x,\frac{1}{2}$	$\bar{x},\bar{x}+\frac{1}{2},\frac{1}{2}$
			$\bar{x},x,\frac{1}{2}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},\frac{1}{2}$	$\bar{x}+\frac{1}{2},\bar{x},\frac{1}{2}$	$x,x+\frac{1}{2},\frac{1}{2}$
8	g	$..2$	$x,\bar{x},0$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},0$	$x+\frac{1}{2},x,0$	$\bar{x},\bar{x}+\frac{1}{2},0$
			$\bar{x},x,0$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},0$	$\bar{x}+\frac{1}{2},\bar{x},0$	$x,x+\frac{1}{2},0$
4	f	$2mm.$	$\frac{3}{4},\frac{1}{4},z$	$\frac{1}{4},\frac{3}{4},z$	$\frac{1}{4},\frac{3}{4},\bar{z}$	$\frac{3}{4},\frac{1}{4},\bar{z}$
4	e	$..2/m$	$0,0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$
4	d	$..2/m$	$0,0,0$	$\frac{1}{2},\frac{1}{2},0$	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$
2	c	$4mm$	$\frac{1}{4},\frac{1}{4},z$	$\frac{3}{4},\frac{3}{4},\bar{z}$		
2	b	$\bar{4}m2$	$\frac{3}{4},\frac{1}{4},\frac{1}{2}$	$\frac{1}{4},\frac{3}{4},\frac{1}{2}$		
2	a	$\bar{4}m2$	$\frac{3}{4},\frac{1}{4},0$	$\frac{1}{4},\frac{3}{4},0$		

Powdercell



H	K	L	2θ / deg	d / Å	I / rel	|F(HKL)|	MU	FWHM
0	0	2	13.594	6.50840	0.14	17.45	2	0.071
1	0	1	23.449	3.79075	1.40	27.23	8	0.071
0	0	4	27.385	3.25420	3.12	81.27	2	0.071
1	0	3	30.528	2.92596	71.32	194.20	8	0.071
1	1	0	31.914	2.80191	13.47	119.35	4	0.071
1	1	2	34.833	2.57356	38.45	142.59	8	0.071
1	0	5	41.468	2.17579	18.76	99.59	8	0.071
0	0	6	41.595	2.16947	3.03	80.09	2	0.071
1	1	4	42.542	2.12330	11.10	76.62	8	0.071
2	0	0	45.759	1.98125	60.30	252.52	4	0.071
2	0	2	47.959	1.89538	0.39	14.41	8	0.071

Extract the reflection list: (hkl) – position - intensity

Preparation of a reflection list for further use

1. Collect a diffraction pattern from the pure phase. If pure phase material is not available, then the phase should constitute the bulk of the sample.
2. Run the Rietveld program in the LeBail fitting mode using the assigned space group and unit cell parameters. From the refined list of intensities, create a file containing h, k, l, M, d, 2θ and I, where h, k and l are the Miller indices of the reflection, M is the reflection multiplicity, d is the d-spacing of the reflection, 2θ is the Bragg angle and I is the reflection intensity.
3. Depending on which Rietveld program has been used, it might be necessary to remove the effect of the Lorentz-polarization (Lp) factor from each observed peak intensity:

$$Lp = \frac{1 + \cos^2 2\alpha \cdot \cos^2 2\theta}{4 \cos\theta \sin^2\theta \cdot (1 + \cos^2 2\alpha)}$$

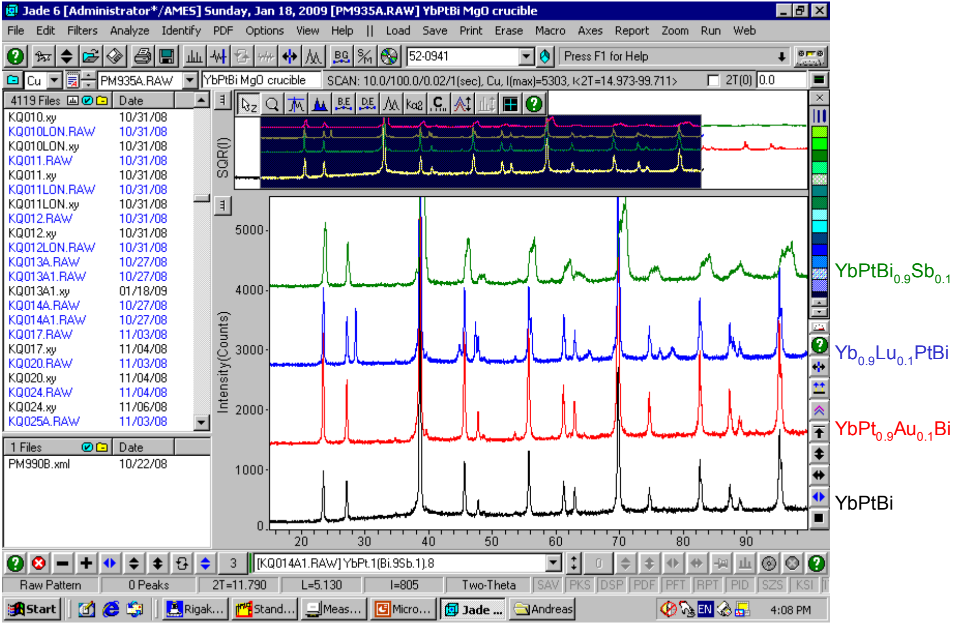
where α is the diffraction angle of the monochromator.

Note that Equation (23) refers to Bragg–Brentano geometry.

4. Removal of the contribution of the Lp factor from the measured intensities *via*:

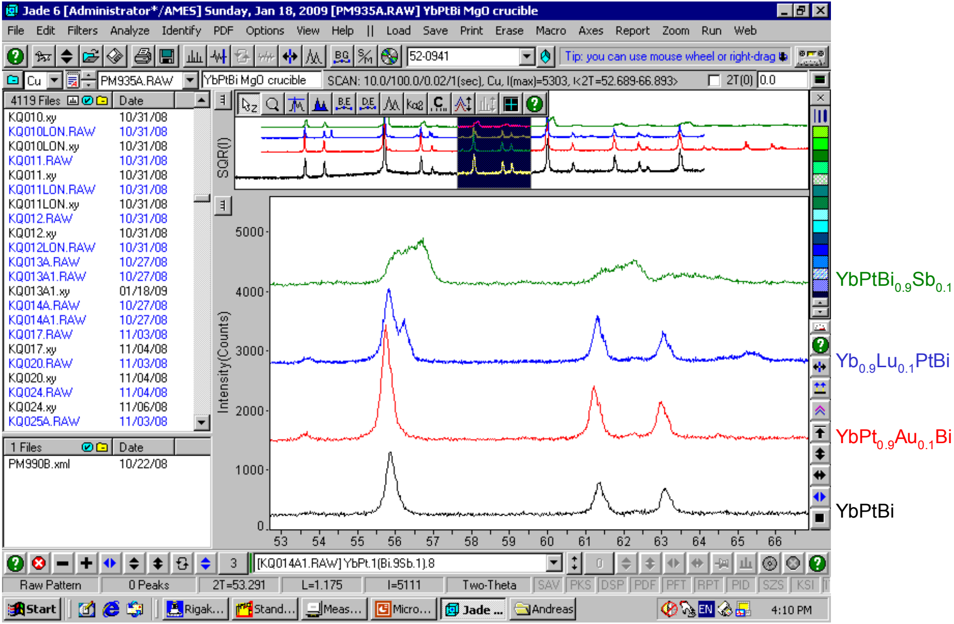
$$I'_{\mathrm{meas}} = \frac{I_{\mathrm{meas}}}{Lp}$$

Example: growth of YbPtBi with partial element substitution



Which phases were grown successfully?

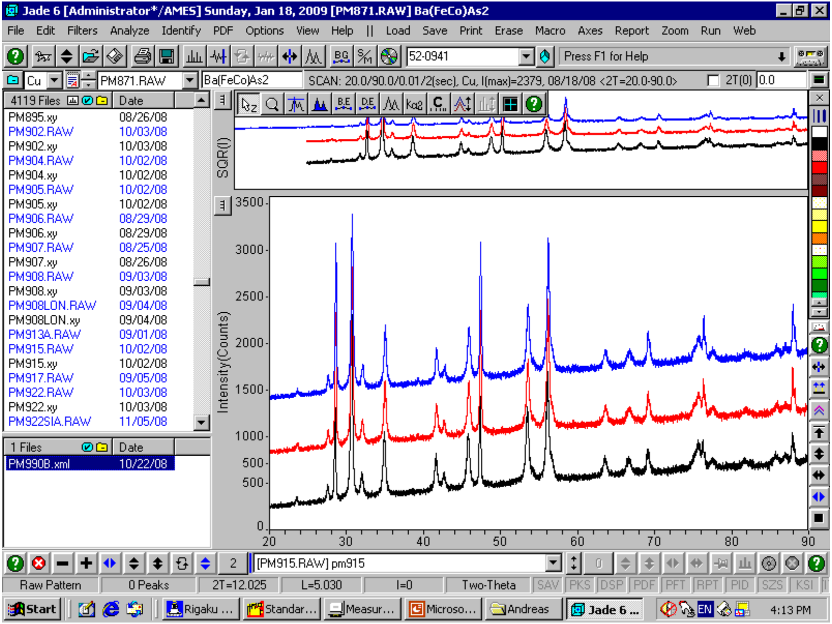
Example: growth of YbPtBi with partial element substitution



Only YbPt$_{0.9}$Au$_{0.1}$Bi was grown successfully.

E. D. Mun: PM935-Ex2c

Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$



x = 0.10

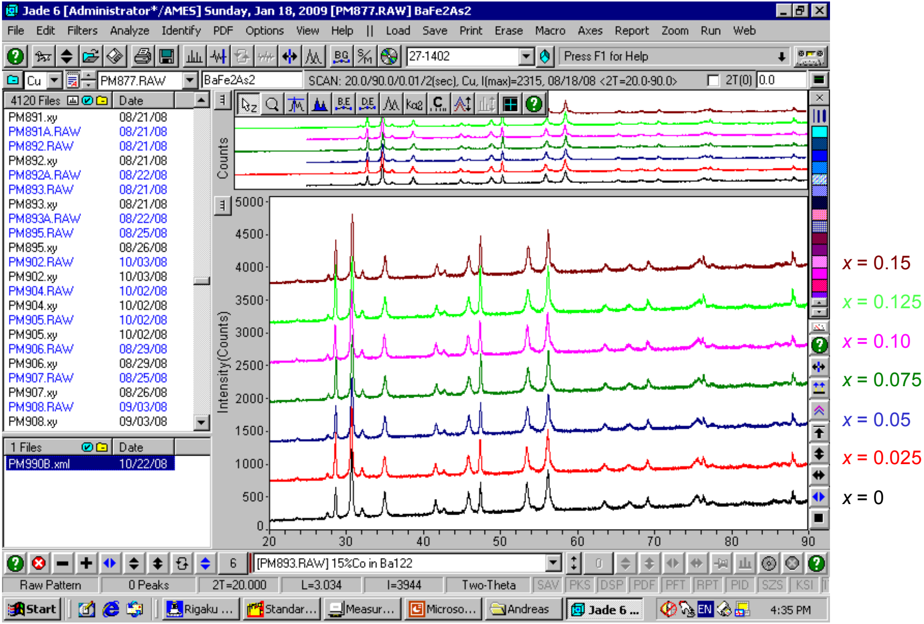
PM915

PM892

PM871

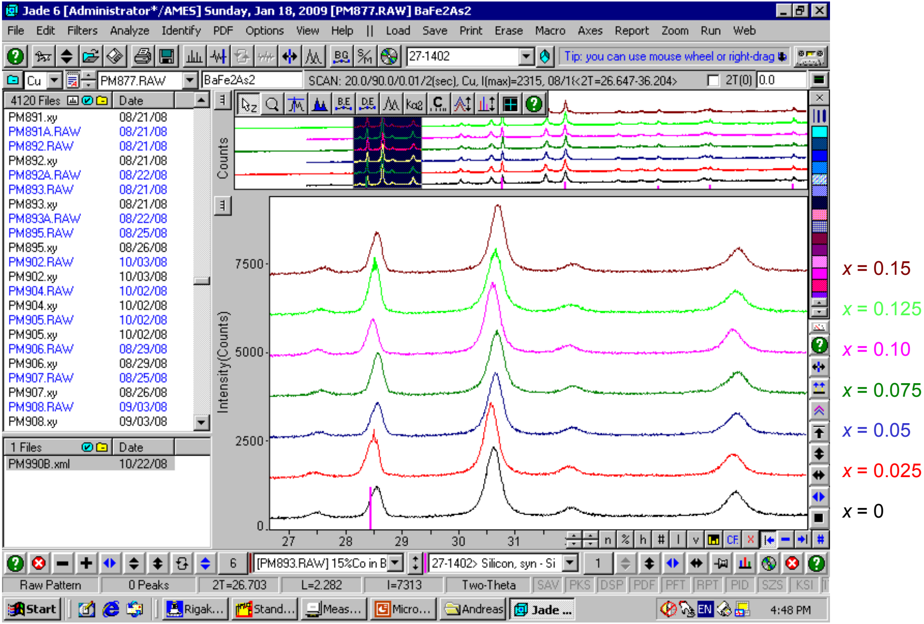
Preparation of samples with same stoichiometry is reproducible.

Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$



Preparation of samples with varying stoichiometry seems also successful.

Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$



Use of “inner” standard a MUST.

N. Ni: PM871-Ex3e

Position of Bragg reflections in powder pattern

$$\lambda = 2d_{hkl}\sin\theta$$

$$\frac{1}{d^2} = \frac{1}{V^2}\left(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{13}hl + 2S_{23}kl\right)$$

$$V = abc\sqrt{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma}$$

$$S_{11} = b^2c^2\sin^2\alpha$$
$$S_{22} = a^2c^2\sin^2\beta$$
$$S_{33} = a^2b^2\sin^2\gamma$$
$$S_{12} = abc^2(\cos\alpha\cos\beta-\cos\gamma)$$
$$S_{13} = ab^2c(\cos\gamma\cos\alpha-\cos\beta)$$
$$S_{23} = a^2bc(\cos\beta\cos\gamma-\cos\alpha)$$

Factors affecting peak positions:

$$\Delta 2\theta = \frac{p_1}{\tan 2\theta} + \frac{p_2}{\sin 2\theta} + \frac{p_3}{\tan\theta} + p_4\sin 2\theta + p_5\cos\theta + p_6$$

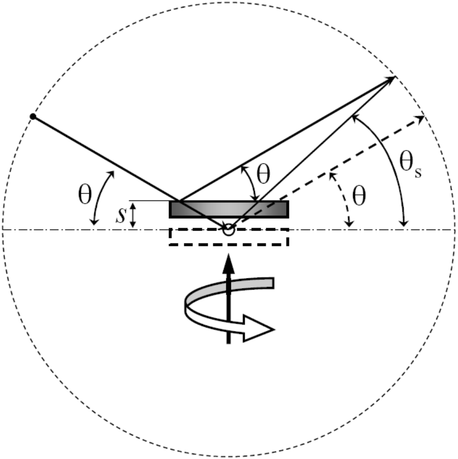
Asymmetry: $p_1 = -\dfrac{h^2K_1}{3R^2}$; $p_2 = -\dfrac{h^2K_2}{3R^2}$

In-plane divergence: $p_3 = -\dfrac{\alpha^2}{K_3}$

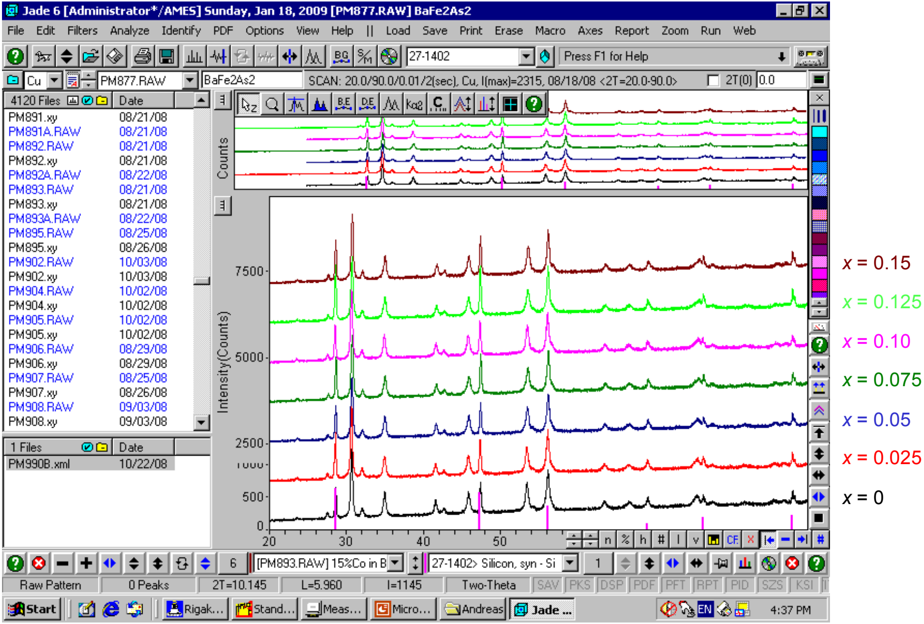
Transparency: $p_4 = \dfrac{1}{2\mu_{eff}R}$

Sample displacement: $p_5 = -\dfrac{2s}{R}$

Zero shift: p_6

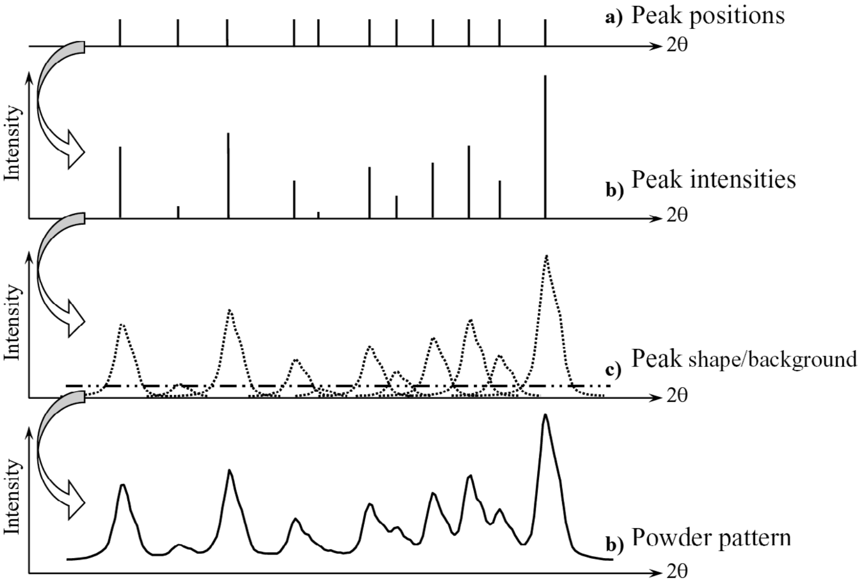


Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$

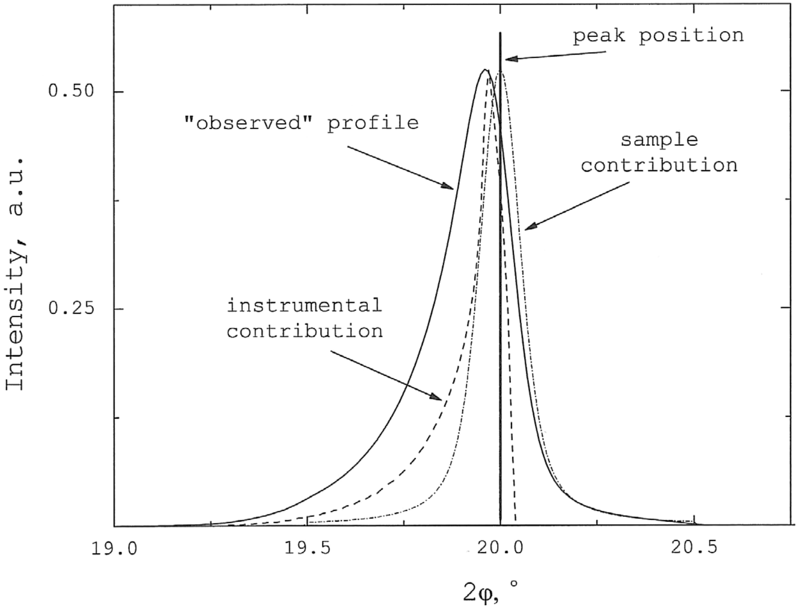


Combined analysis of series of Bragg reflections (main phase + standard) necessary.

Combined fitting of Bragg reflections



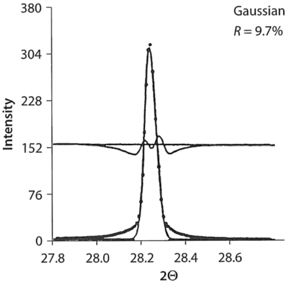
Profile of Bragg reflections in powder pattern

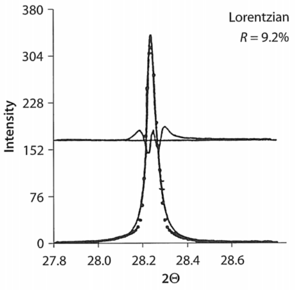


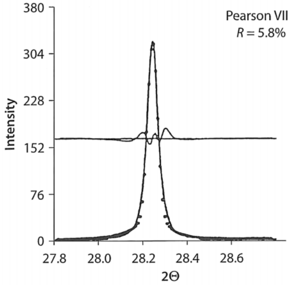
Profile of Bragg reflections in powder pattern

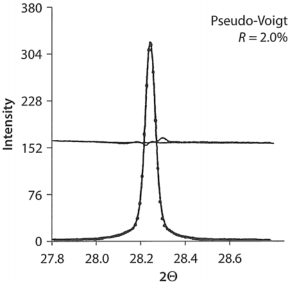
Gaussian	$G = I_0 \exp\left(-\ln 2\left(\frac{2\Theta - 2\Theta_0}{\omega}\right)^2\right)$
Lorentzian	$L = I_0\left(1+\left(\frac{2\Theta - 2\Theta_0}{\omega}\right)^2\right)^{-n}$ $\quad n = 1; 1.5; 2$
Pseudo-Voigt	$V = \eta L + (1-\eta)G \qquad (0 \le \eta \le 1)$
Pearson VII	$P = I_0\left(1+\left(\frac{2\Theta - 2\Theta_0}{ma^2}\right)^2\right)^{-m}$

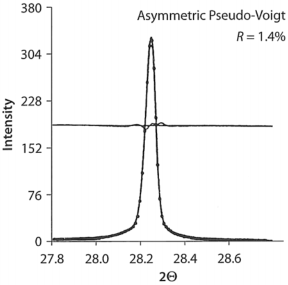
Parameter: $2\Theta_0$ = peak position; I_0 = peak intensity; $\omega = FWHM/2$; m = shape parameter.











Will 23; 80_1,2; 81_1,2,3

R-values (residuals) – reliability criteria for refinements

$$R = \frac{\sum_i \left| y_i(\text{obs}) - y_i(\text{calc}) \right|}{\sum_i \left| y_i(\text{obs}) \right|}$$

$$R_{wp} = \frac{\sqrt{\sum_i w_i \left(y_i(\text{obs}) - y_i(\text{calc}) \right)^2}}{\sqrt{\sum_i w_i y_i(\text{obs})^2}} \qquad R_{\text{exp}} = \frac{\sqrt{n-m}}{\sqrt{\sum_i w_i y_i(\text{obs})^2}}$$

$$M = \left(\sum_i w_i \left(y_i(obs) - y_i(calc) \right)^2 \right)^{1/2}$$

$$R_{Bragg} = \frac{\sum_j \left| I_j(\text{obs}) - I_j(\text{calc}) \right|}{\sum_j \left| I_j(\text{obs}) \right|}$$

Will 115; 120_1,2,3; 121

Example: growth of $Ba(Fe_{1-x}Co_x)_2As_2$

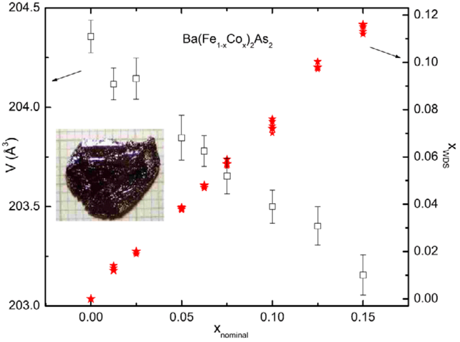


FIG. 2. (Color online) Unit-cell volume and Co concentration determined from WDS measurement as a function of nominal Co concentration. Multiple WDS data points were collected for each nominal x and are each plotted, giving a sense of measured variation in Co concentration. Inset: picture of a representative single crystal over a millimeter grid.

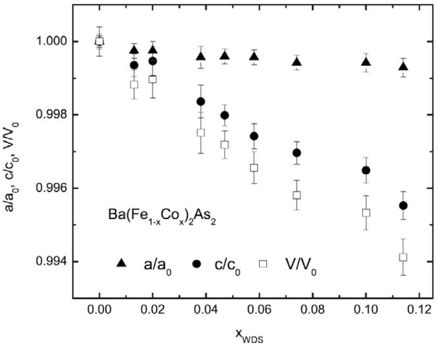
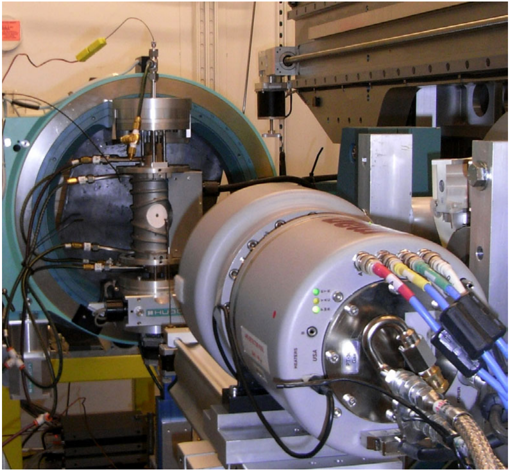


FIG. 3. Unit cell parameters, a and c, as well as unit-cell volume, V, normalized to a_0=3.9621 Å, c_0=13.0178 Å, and V_0 =204.3565 Å^3 of undoped $BaFe_2As_2$ as a function of measured concentration of Co, x_{WDS}.

Realized stoichiometry by WDS study; Vegard's law for lattice parameter

NNi_PhysRevB_78_214515 2; 3

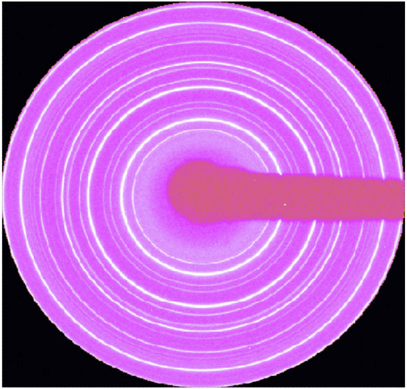
Example: preparation of *R*FeAs(O/F)

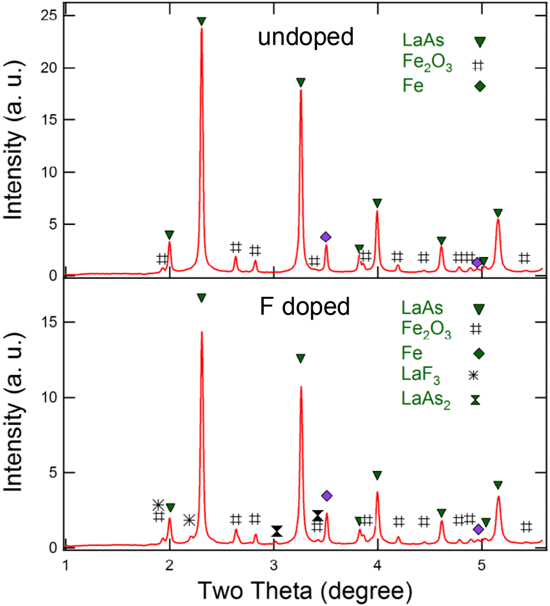


High-temperature x-ray diffraction with 2-dimensional detector

Rimg3307; 3318

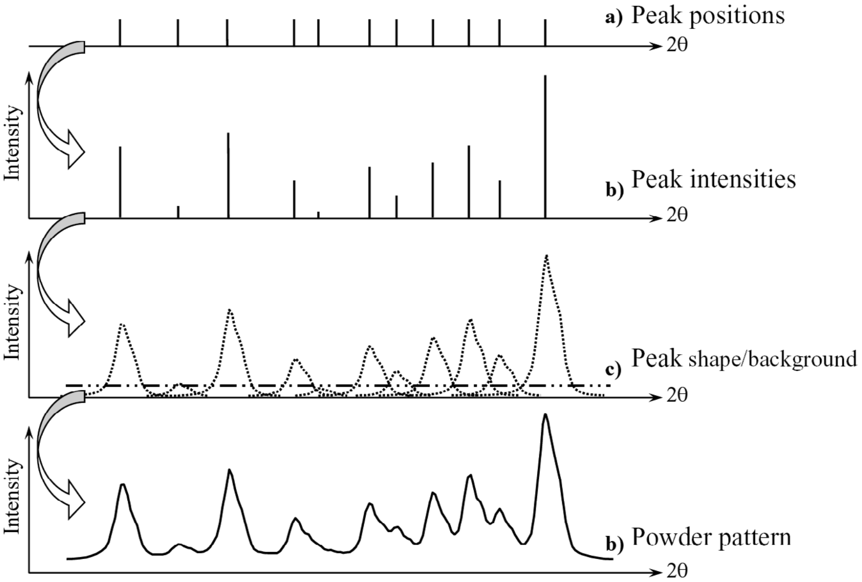
Example: preparation of *R*FeAs(O/F)





High-temperature x-ray diffraction with 2-dimensional detector

Rietveld refinement of powder pattern



Intensity of Bragg reflections in powder pattern

$$I_{hkl} = K \times p_{hkl} \times L_\theta \times P_\theta \times A_\theta \times T_{hkl} \times E_{hkl} \times \left|F_{hkl}\right|^2$$

Structure amplitude:

$$\mathbf{F(h)} = \sum_{\mathrm{j}=1}^{n} g^{\mathrm{j}} t^{\mathrm{j}}(s) f^{\mathrm{j}}(s) \exp(2\pi \mathbf{i}\mathbf{h} \cdot \mathbf{x}^{\mathrm{j}})$$

K = scale factor

p_{hkl} = multiplicity factor

L_θ = Lorentz factor

P_θ = polarization factor

A_θ = absorption factor

T_{hkl} = preferred orientation factor

E_{hkl} = extinction factor

g^{j} = population

t^{j} = Temperature factor

Lorentz and Polarization factor

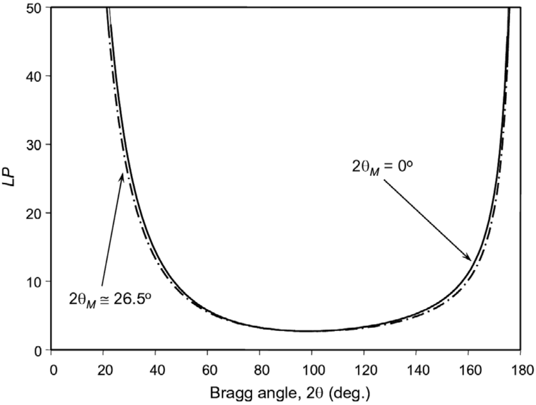
L_θ = Lorentz factor

$$L = \frac{1}{\cos\theta \sin^2\theta}$$

P_θ = polarization factor

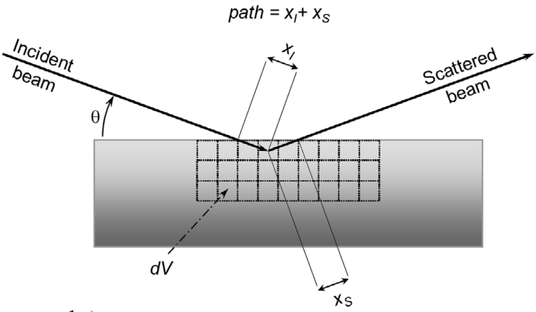
$$P \propto \frac{1 - K + K\cdot\cos^2 2\theta \cdot \cos^2 2\theta_M}{2}$$

$$LP = \frac{1 + \cos^2 2\theta \cos^2 2\theta_M}{\cos\theta \cdot \sin^2\theta}, K{=}0.5$$



Absorption factor

$$A_\theta = \text{absorption factor}$$



$$A = \frac{1}{V}\int_V \exp(-\mu_{eff}\, l)\, dV$$

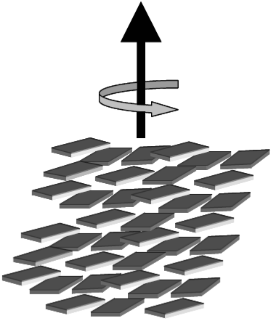
$$A = \frac{\mu_{eff}}{2} = \text{const (flat opaque sample)}$$

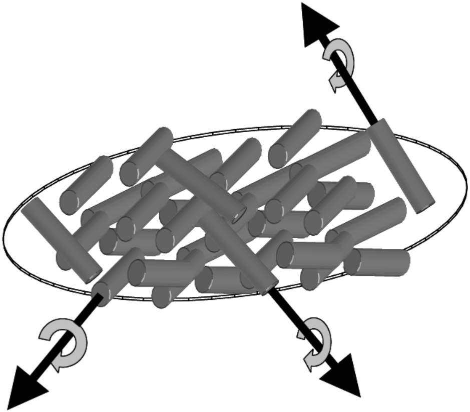
$$A = \frac{1-\exp(-2\mu_{eff}\, t/\sin\theta)}{2\mu} \propto 1-\exp(-2\mu_{eff}\, t/\sin\theta)$$

flat semitransparent sample

Preferred orientation factor

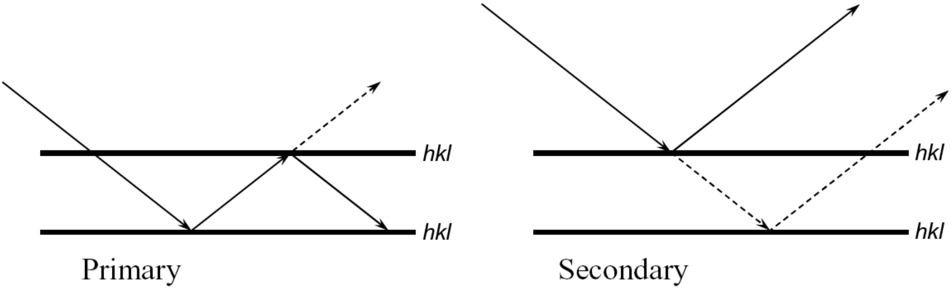
T_{hkl} = preferred orientation factor





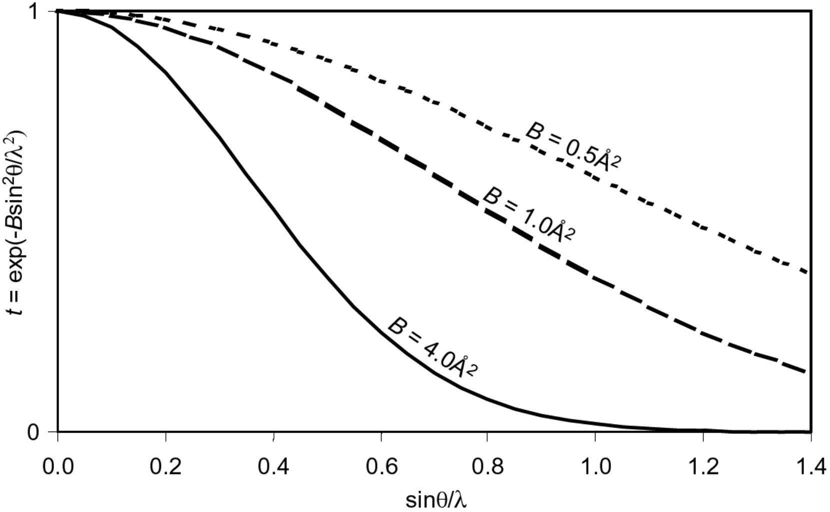
Extinction factor

E_{hkl} = extinction factor



Temperature factor

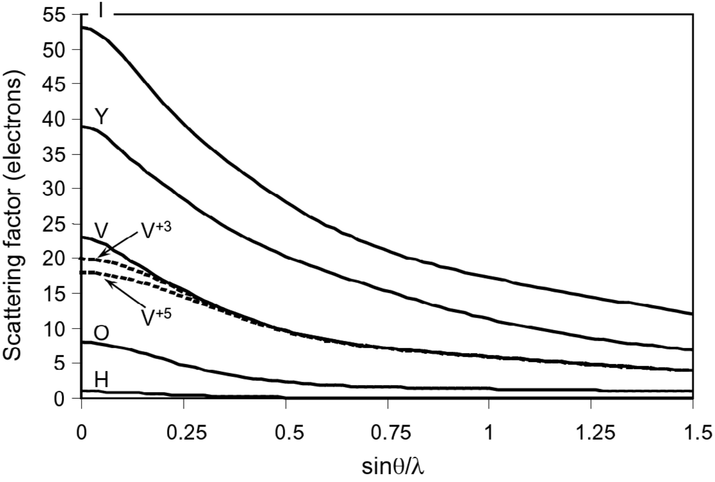
Temperature factor: $$t^{j} = \exp\left(-B^{j}\frac{\sin^{2}\theta}{\lambda^{2}}\right)$$ (isotropic)



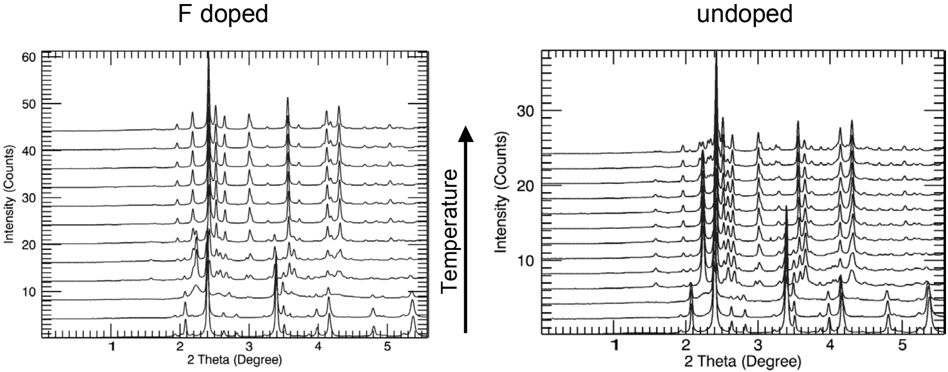
Atomic scattering factor

f^j = atomic scattering factor (radial distribution of electrons for x-rays), constant for neutrons

Units: Scattering ability of a single electron
Coherent scattering length. Femtometer = 10^{-15}m

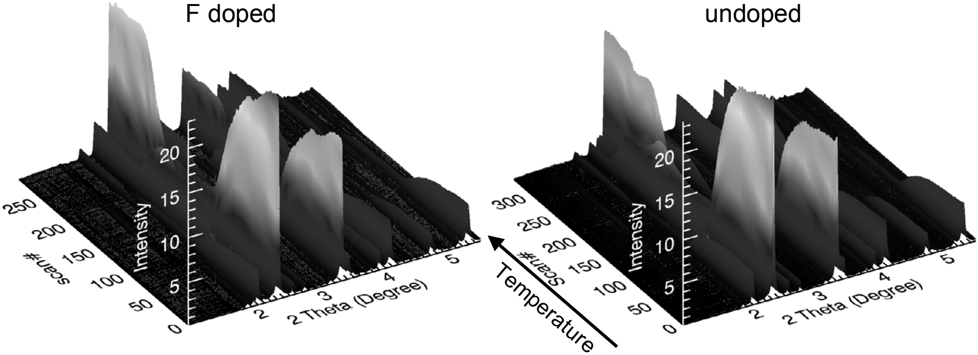


Example: preparation of *R*FeAs(O/F)



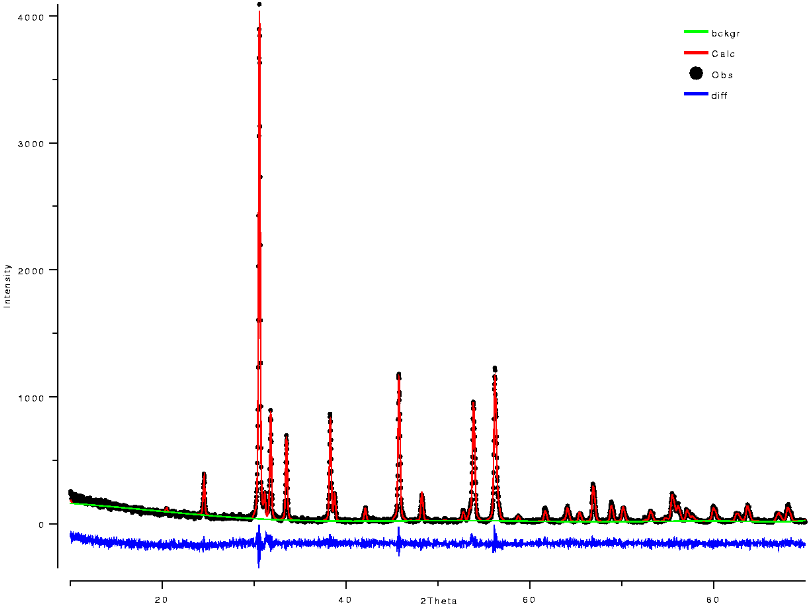
Temperature-dependent x-ray diffraction (20 sec. pattern)

Example: preparation of *R*FeAs(O/F)



Temperature-dependent x-ray diffraction (20 sec. pattern)

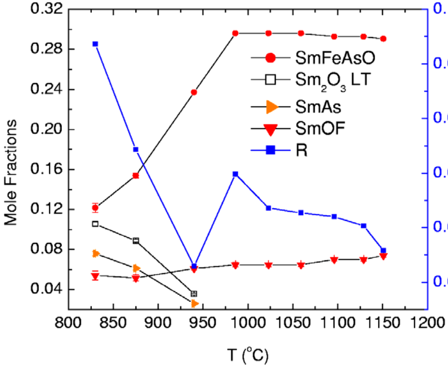
Example: preparation of *R*FeAs(O/F)



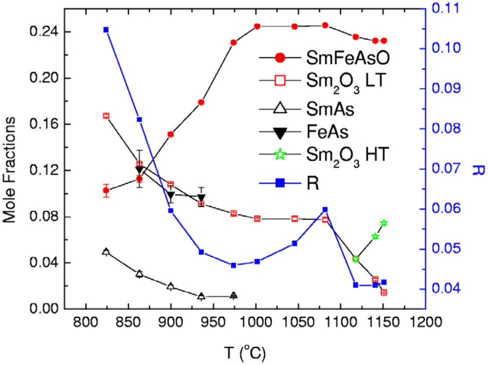
Multi-phase Rietveld refinement

Example: preparation of *R*FeAs(O/F)

F doped

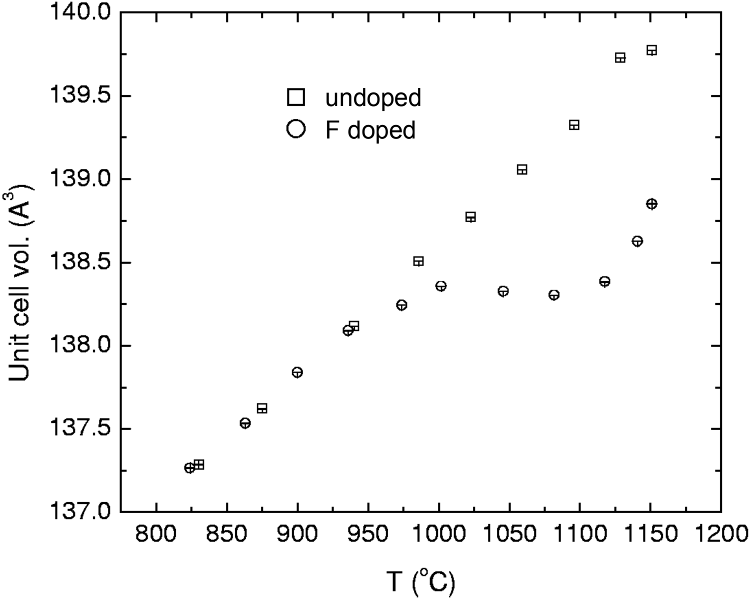


undoped



Crystalline phase fraction determined by Rietveld analysis

Example: preparation of *R*FeAs(O/F)



Unit-cell volume of *R*FeAs(O/F) phase determined by Rietveld analysis

Why and when powder for structure determination?